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Performance study in the hydrotreatment of coal with coal-derived solvents

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ABSTRACT

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Hydrotreatment of coal in the presence of hydrogen donor solvents is considered to be a potential route for developing value-added carbon products. The aim of this research was to investigate the use of coal-derived solvents as replacements for expensive hydrogen-donor solvents like tetralin, in the production of hydrogen rich carbon products. Three coal-derived solvents obtained from the metallurgical coke ovens, namely Heavy Creosote Oil (HCO), Carbon Black Base (CBB) and Refined Chemical Oil (RCO), were utilized as hydrogen donor solvents in the hydrotreatment process. The coal-alone conversion in producing THF solubles decreased in the order as CBB>HCO>RCO. Process-derived (recovered) solvents were isolated as vacuum distillation overheads and tested for their effectiveness towards producing THF solubles. The coal-alone conversion for these recovered was found to be comparable to the starting fresh solvents. An average mass loss of 7-10 % was observed for the fresh solvents whereas the mass loss increased slightly to 10-13 % for the recovered solvents during the hydrotreatment runs. The residue from the vacuum distillation i.e. the pitch, was characterized by testing for softening point, ash content, elemental analysis and optical texture. The coke yield and softening point of the pitch followed a linear dependence on the amount of solvents distilled from the product mixture. The effect of temperature and reaction atmosphere was also studied on the hydrotreatment process. The coal-alone conversion increased with higher temperature and a hydrogen atmosphere was found to be crucial. The optimum process temperature was found to be 450 ^{o}C under 500 psig hydrogen pressure. Reaction conditions did not affect the recovered solvent performance upon recycle in producing THF solubles. The ash content of the pitches was found to be low i.e 0.2 %. The optical texture of the cokes was found to have an anisotropic structure. The elemental composition of the pitches showed higher hydrogen-to-carbon ratio than the starting coal and was found to be similar irrespective of reaction conditions. Finally, successive use of only recovered solvents and/or blends of fresh and recovered solvents were studied to mimic a continuous hydrotreament operation. The coal-alone conversion decreased after going through a maximum in both the cases. While the decreasing trend continued for the pure recovered solvents, the coal-alone conversion was found to stabilize for the blends.

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CHAPTER 1
INTRODUCTION

The element carbon is the building block of life. Carbon is the major chemical constituent of most organic matter, from fossil fuels to the complex molecules like DNA and RNA that control genetic reproduction in organisms. Carbon (C) is the fourth most abundant element in the Universe, after hydrogen (H), helium (He), and oxygen (O). The concentration of carbon in the Earth is only 0.19 %. The Earth's crust is only 0.032 % carbon by weight [7].

Carbon is stored on earth in the following major sinks: (1) as organic molecules in living and dead organisms in the biosphere; (2) as the gas carbon dioxide in the atmosphere; (3) as organic matter in soils; (4) in the lithosphere (Earth's crust) as fossil fuels and sedimentary rock deposits such as limestone, dolomite and chalk; and (5) in the oceans as dissolved atmospheric carbon dioxide and as calcium carbonate shells in marine organisms. Carbon is stored in the lithosphere in both inorganic and organic forms. Inorganic deposits of carbon in the lithosphere include fossil fuels like coal, oil, and natural gas, oil shale, and carbonate based sedimentary deposits like limestone. Organic forms of carbon in the lithosphere include litter, organic matter, and humic substances found in soils.

The element carbon is used in the production of many materials. Examples of such materials are plastics, pharmaceuticals, iron, steel and aluminum. Half of the carbon found in the lithosphere is in a non-reactive form, such as carbon dioxide and carbonate materials. The remainder of the carbon is concentrated in various fossil fuels, including

coal, petroleum, and natural gas. These fossil fuels are the predominant source of energy and feedstock for the production of chemicals in the world today [16].

There are three major forms of fossil fuels: coal, oil and natural gas. All three were formed many hundreds of millions of years ago before the time of the dinosaurs-hence the name fossil fuels. The time from over which most fossil fuels were formed encompass the Carboniferous, Mesozoic and the Cenozoic periods, which are a part of the Paleozoic era. "Carboniferous" gets its name from carbon, the basic element in coal and other fossil fuels.

The major use of fossil fuels is in the production of heat by combustion. These fossil fuels are also extremely important in their non-fuel uses. Coal can be used to satisfy the needs of a modern industrial civilization. These needs include not only the generation of electricity and transportation fuels, but also cokes for extracting metals from their ores, chemicals including plastics, medicines, and fertilizers etc. Though some of the above uses can be satisfied by coal, petroleum is preferred in some cases over coal due to its liquid state making it easy to process and transport and also due to the premium quality of the products obtained from it. Currently, products derived from petroleum dominate the non-fuel uses of fossil fuels [16]. These products include the production of petrochemicals, asphalt and road tar, waxes, liquefied petroleum gases, and petroleum coke and pitch. Coal on the other hand has several advantages over petroleum. Petroleum reserves are declining rapidly, and the concentration of impurities such as sulfur, vanadium, and nickel, in the petroleum reserves is on the rise. The known reserves of coal are expected to significantly outlast those of petroleum by centuries. This has led to

an increased research in replacing coal over petroleum for developing fuels, chemicals and value-added carbon materials from coal.

Currently, several non-fuel uses of coal include high-temperature carbonization for the production of metallurgical coke, coal tar, and coal tar pitch, gasification to produce synthesis gases, liquefaction to produce liquid fuels, chemicals and carbon materials etc. Most carbon-product feedstocks from coal are by-products from the metallurgical coke industry. During the process of high temperature carbonization or coke making, the volatiles are captured and condensed to yield coal tar. The coal tar can then be processed by distillation and separated into various fractions to get carbon feedstocks such as tar acids, tar bases, naphthalene, creosote oils, and coal tar pitch. Coal tar pitch is defined as the solid residue remaining after the removal of low molecular weight volatiles from coal tar by distillation. This pitch has many different uses in industry today. It is used as a binder in the production of graphite electrodes for electric furnaces and carbon anodes for the aluminum industry. Coal tar pitch can be used to impregnate carbon artifacts when high density and strength are necessary. It can also be used as a carbon feedstock for the production of carbon fibers, specialty graphite, carbon composites, carbon foams, carbon nanofibers and nanotubes.

The disadvantage to the use of coal tar pitch is that it is derived as a by-product of the metallurgical coke making industry. The amount of coal tar produced from one ton of coal is on the order of 4 wt% of the original coal. Moreover, coal tar pitch accounts for only approximately 50 wt% of coal tar, or approximately 2 wt% of the original coal [25]. This disadvantage is magnified by the fact that the production of metallurgical coke by carbonization is declining in the United States by 3-4% per year due to increased imports,

decreasing coke demand, and environmental regulations placed on existing coke ovens [1]. In order to compensate for the decrease in pitch derived from coal tar and the dwindling supply and quality of petroleum, these precursors for carbon products could be produced directly from coal as primary products. One route to the production of carbon product precursors from coal is through the liquefaction of coal. Two general methods of liquefaction are commonly practiced today: direct and indirect liquefaction. Indirect liquefaction converts coal into synthesis gas: carbon monoxide and hydrogen. These gases are then reformed to produce various hydrocarbons. In direct liquefaction, or hydrogenation, coal is thermally treated in the presence of hydrogen and/or a hydrogen-rich donor solvent to produce low molecular-weight organic species. These low molecular organic species can be either liquid and/or solid based on the processing conditions and hydrotreatment. The liquids obtained are hydrogen rich aromatic hydrocarbons, whereas the solid can form a precursor to a gamut of carbon products like binders, impregnators, cokes, fibers, foams etc.

Coal-derived pitches have been obtained by combining coal hydrogenation and solvent extraction [34, 35]. In these experiments, coal is hydrogenated in the presence of tetralin. This solvent has been proven to be a very effective hydrogen donor in the presence of coal. However, during liquefaction reactions, tetralin is converted into naphthalene and cannot be reused without external separation and rehydrogenation. Also tetralin is an expensive solvent and cannot be employed for commercial production of pitches because its cost far exceeds the cost of the final carbon product.

Coal-derived liquids could replace tetralin as the liquefaction solvent. Making this substitution would have several advantages: (1) the possibility of producing a

recyclable solvent during the product separation steps thus eliminating the need to supply an external solvent except for makeup; (2) the process would employ only coal and coal products as starting materials, thus generating a completely coal-derived carbon product precursor; (3) the coal-derived liquids are by-products from the coal tar industry and their low cost compared to tetralin would significantly bring down the overall process cost, making it an economically viable process. As mentioned earlier, these coal-derived liquids come from the by-product coke oven industry and since the coke industry is on a decline, the availability of these coal-derived liquids may become a problem. Nevertheless except for this problem, the advantages seem to promise a future for these liquids, so it is worthwhile to study these coal-derived liquids as liquefaction solvents. The evaluation of several coal-derived liquids as liquefaction solvents for the production of carbon-product precursors is studied in this research. In addition, the recycle of the recovered solvents was investigated for its effectiveness towards digesting coal, so that the need for providing external solvents is minimized during a continuous hydrogenation process.

1.1 Proposed Research

Three different coal-derived liquids have been collected for testing as hydrogen-donor solvents in order to produce precursors for carbon products. All of the three liquids namely Heavy Creosote Oil (HCO), Carbon Black Base #1 (CBB), and Refined Chemical Oil (RCO) are obtained from Koppers Industries, Inc. in Pittsburgh, Pennsylvania. All of these liquids are distillate fractions of coal tar derived from the production of metallurgical coke.

The first step of this research is the evaluation of these coal-derived liquids for their ability to produce a THF soluble product from coal, called pitch, which can act as a carbon- product precursor. In the second step, products of the hydrotreatment reactions are separated into three different fractions: unconverted coal, carbon pitch, and a recycle solvent. The main focus of this research is to study the recycle solvent from the coal hydrotreatment reaction for its ability to produce more pitch material upon subsequent reaction with coal. The results obtained with hydrotreatment of coal by the recycle solvent will be compared to those obtained with hydrotreatment of coal by fresh solvent. The ultimate objective would be to make the hydrotreating process continuous without addition of any external fresh solvent.

The resultant carbon pitch is tested as a precursor to carbon products. This was done using standard test procedures such as softening point, ash determination, coking value, and optical texture. Using these parameters, the products from the hydrotreatment of coal can be compared to cokes and pitches of commercial value today.

1.2 Research Scope

The scope of research is divided into the following tasks:

- Evaluate the three different solvents HCO, CBB, RCO for their ability to convert coal into pitch material by determining the conversion yield to pitch, i.e. THF soluble products.
- Separate the solvent from the pitch material by vacuum distillation and use it as a recycle solvent for subsequent hydrotreatment reactions.

- Investigate the efficiency of these recycled solvents by determining the conversion yield to pitch and compare this to the conversion yield obtained using fresh solvents.
- Investigate the effect of temperature and gas phase atmosphere on conversion yields for both fresh and recycled solvents.
- Investigate the conversion effectiveness of successive recovered solvents with and without addition of any fresh solvent.
- Test the resultant coal-derived pitches for coke yield, softening point, ash content and optical properties to determine their potential as carbon-material precursors.

CHAPTER 2

BACKGROUND

In this chapter, a review of basic concepts is presented which defines the art of producing carbon products directly from coal. One must have some insight into basic knowledge of coal, including its formation, composition, classification, and structure. A brief description of these aspects is included. Several different methods of processing coal, such as pyrolysis, indirect liquefaction, and direct liquefaction are discussed here. A review regarding the parameters affecting coal conversion during hydrotreatment and possible mechanisms by which these reactions might take place is presented. Some of these parameters are relevant to this research as they were studied to see how they affect the process of hydrotreatment of coal. Finally the products that can be obtained from coal processing and some characterization techniques are also described.

2.1 Coal – Formation, Composition and Classification

Coal formation involves two different stages, the biochemical stage and the geochemical stage. The biochemical stage begins with the formation of peat beds as plant material settles under water in low, swampy areas. At this stage, bacteria and fungi begin to decompose the plant material by removing oxygen and hydrogen and giving off water, carbon dioxide, and methane. The biochemical stage of coal formation ends as more and more sediment begins to cover the peat layer. As the peat is further submerged

and the sediment layer gradually increases to approximately 40 centimeters, bacteria and fungi cease to exist, thus ending the biochemical stage [20].

The second stage of coalification is the geochemical stage. During this stage, the peat bed undergoes further decomposition due to the elevated temperature and pressure from further layers of sediment depositing on top of the peat bed. Oxygen and hydrogen are again eliminated as methane, carbon dioxide and water. As this proceeds, the carbon content is slowly increased. Depending on the time, temperature and pressure to which the coal is subjected, different degrees of coalification or ranks that vary from anthracite through bituminous and sub-bituminous coal to lignite are obtained.

Anthracite is the highest or most mature rank of coal, while lignite is the lowest rank coal. The American Society for Testing and Materials (ASTM) classifies coal by the amount of fixed carbon or volatile matter for medium-volatile bituminous through anthracite. The lower ranked coals, lignite through high-volatile A bituminous, are ranked by their heating value and agglomerating character. The ASTM classification is shown in Table 2.1.

With the amount of carbon decreasing with decreasing rank, other elements like hydrogen and oxygen must increase in concentration, but the nitrogen and sulfur content vary little with rank. Instead, the content of the nitrogen and sulfur depends on the location where the coal was formed. The elemental composition of coal of varying rank is shown in Table 2.2. It can be seen that as coal rank decreases, the hydrogen-to-carbon ratio increases. Also, the amount of oxygen decreases compared to carbon with increasing rank. All of these elements are bonded together to form various aromatic rings, aliphatic chains, and a wide range of functional groups.

Table 2.1 The ASTM system for classifying coals by rank [15]

Class	Group	Fixed	Volatile	Heating
Anthracite	Metaanthracite	>98	<2	
	Anthracite	92-98	2-8	
	Semianthracite	86-92	8-14	
Bituminous	Low-volatile	78-86	14-22	
	Medium-volatile	69-78	22-31	
	High-volatile A	<69	>31	>14,000
	High-volatile B			13,000-14,000
	High-volatile C			10,500-13,000
Sub bituminous	Sub bituminous A			10,500-11,500
	Sub bituminous B			9,500-10,500
	Sub bituminous C			8,300-9,500
Lignitic	Lignite A			6,300-8,300
	Lignite B			<6,300

Note: This classification system is based on ASTM standard D 388-66, which is published annually by ASTM in their compilation of standards. [a] The fixed carbon and volatile matter, reported as percentages, are determined on a dry, mineral-free basis. The mineral matter is calculated from the ash content by the Parr formula: mineral matter=1.08 [percent ash +0.55 (percent sulfur)] [b] The heating value, reported in British thermal units per pound, is expressed on a moist, mineral-free basis.

Most of the functional groups that are present in coal are those that include oxygen, like phenols, alcohols, ethers, carboxylic acids, and carbonyls. A complex model of a basic coal structure was proposed by Wiser [23] based on the relative abundance of each atom and functional group. This model is shown in Figure 2.1, in which weak bonds in the coal structure are identified by the arrows. Coal liquefaction and dissolution requires breaking the molecular structure of coal into small soluble fragments at these weak bonds.

Table 2.2 Typical percent elemental composition of various coal ranks [3]

Sample	**Element, %wt (dry ash-free basis)**				
	C	**H**	**O**	**N**	**S**
Meta-anthracite	97.9	0.21	1.7	0.2	-
Anthracite	95.9	0.89	1.8	0.3	1.8
Anthracite	92.8	2.7	2.9	1.0	0.6
Semianthracite	90.5	3.9	3.4	1.5	0.7
Low volatile bituminous	90.8	4.6	3.3	0.7	0.6
Medium volatile bituminous	89.1	5.0	3.6	1.7	0.6
High volatile A bituminous	84.9	5.6	6.9	1.6	1.0
High volatile B bituminous	81.9	5.1	10.5	1.9	0.6
High volatile C bituminous	77.3	4.9	14.3	1.2	2.3
Subbituminous A	78.5	5.3	13.9	1.5	0.8
Subbituminous B	72.3	4.7	21.0	1.7	0.3
Subbituminous C	70.6	4.8	23.3	0.7	0.6
Lignite	70.6	4.7	23.4	0.7	0.6

Petroleum and coal have been competitors in producing value-added carbon products. However, petroleum is usually preferred over coal, due to its liquid form and the nature of the properties of the products. In order for coal to be considered as a possible precursor to high-value carbon products, its products must have properties similar to that of petroleum. It is necessary to understand some of the key differences between the structure of coal and oil. The major difference between coal and oil is that the molecular weight of crude oil has a range of 150 to 250 [10], while the average molecular weight of coal usually exceeds 1000. Another major difference between coal and oil is that on average the atomic hydrogen-to-carbon ratio for coal is much lower than that of oil. The typical value for crude oil lies between 1.4 and 1.9, while the average

value for coal is only about 0.8 [17]. For comparison, a list of typical hydrogen-to-carbon atomic ratios for several coals and hydrocarbons is given in Table 2.3.

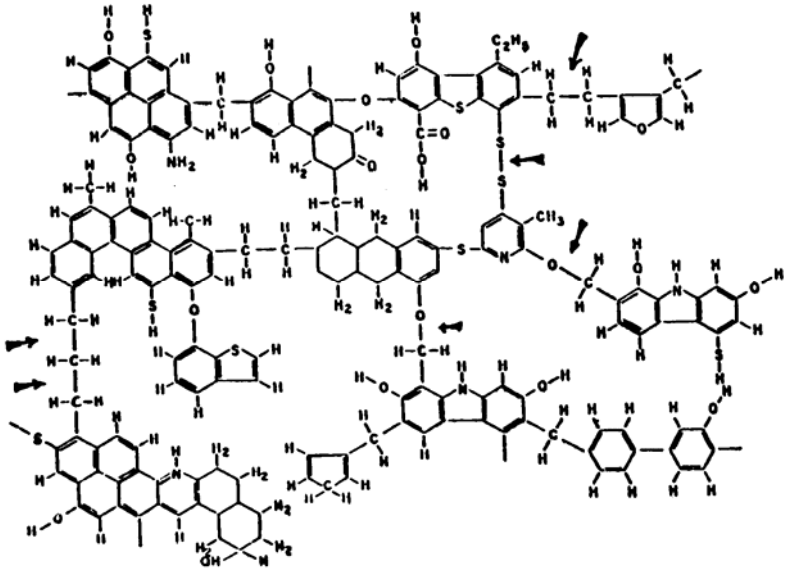


Figure 2.1 One typical molecular unit in coal [23]

The original hydrogen-to-carbon ratio must be increased in order for coal products to be comparable to those obtained from petroleum, in terms of liquid fuels. There are two different ways of performing this task: the addition of hydrogen or the rejection of carbon. These two methods are the basis for most coal conversion processes. There are four chief processes that are included here: pyrolysis or carbonization, indirect liquefaction or gasification, and direct liquefaction with catalysts (catalytic hydrogenation) and without a catalyst (dissolution or solvent extraction) [9]. These conversion schemes are shown in Figure 2.2.

Table 2.3 Typical compositions of coals and liquid hydrocarbons[a] [9]

Element	Anthracite	mv Bit.	hvb Bit.	Lignite	Asphaltene	Toluene	Petroleum Crude	Gasoline	Methane
C	93.7	88.4	80.3	72.7	87	91.3	83.0-87.0	86	75
H	2.4	5	5.5	4.2	6.5	8.7	11.0-14.0	14	25
O	2.4	4.1	11.1	21.3	3.5				
N	0.9	1.7	1.9	1.2	2.2		0.2		
S	0.6	0.8	1.2	0.6	0.37		1		
H/C Ratio	0.31	0.67	0.82	0.69	0.9	1.14	1.76	1.94	4

[a] Coal analysis on moisture- and ash-free basis; ash content of coal 3-15 %

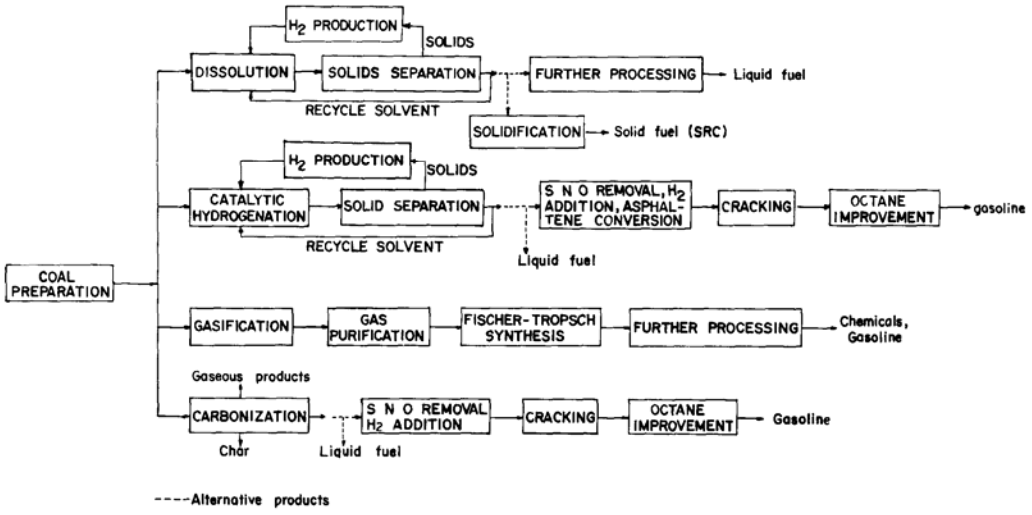


Figure 2.2 Alternate routes for coal liquefaction [9]

2.2 Pyrolysis

Pyrolysis or carbonization is shown as the bottom process in Figure 2.2. This technique employs the approach of rejecting carbon as its method of increasing the hydrogen-to-carbon ratio of raw coal. Pyrolysis takes place as coal is thermally treated in the absence of oxygen to form hydrogen rich liquids and gases and a carbon rich residue, termed either char or coke. This is done in the absence of oxygen, so that combustion reactions do not take place. This is the one method whereby a large number of carbon atoms are rejected as solids, with the liquid and gaseous products containing a much higher hydrogen/carbon ratio. Depending upon the temperature of operation, coal carbonization processes can be classified into two types: (1) Low temperature carbonization carried out at 500-700 ^{o}C and (2) High temperature carbonization carried out at temperatures in excess of 700 ^{o}C. The latter is employed for the manufacture of metallurgical coke as a main product while coal tar is also produced as a side product. The liquid products, or coal tar, formed from the condensed volatile matter, can be processed further by hydrogenation and desulfurization to create valuable products. These can be used as feedstocks for the production of dyes, plastics, synthetic fibers, pharmaceuticals, solvents and pitches. The quantities of gas, liquid, and char produced depend on the type of coal, the rate of heating, the nature of gas atmosphere surrounding the coal, and the ultimate temperature achieved.

2.3 Indirect Liquefaction or Gasification

Indirect liquefaction or gasification employs the approach of adding hydrogen as its method of increasing the hydrogen/carbon ratio. In this technique coal is completely

broken down into gaseous products, predominantly carbon monoxide and hydrogen, known as synthesis gas. The general process for indirect liquefaction is shown as the third approach in Figure 2.2. In order for the gasification to take place, coal is usually reacted with steam and oxygen to produce carbon monoxide and hydrogen. Since the complete breakdown of coal structure is desired, the gasification conditions are severe. Typical operating temperature vary between 800-1500 K and pressures between a few to 100's of atmospheres. The synthesis gas generated from coal can then be reformed in the presence of a Fischer-Tropsch catalyst to form various higher hydrocarbons [9]. Also, depending on the choice of Fisher-Tropsch catalyst, the products can be highly selective to hydrocarbon liquids like gasoline, kerosene, diesel fuel, and fuel oil. Products such as methanol and acetone can also be produced depending on the specific type of catalyst. Several types of commonly used catalysts are Fe, Co, Ni, Ru and ZnO_2. Also, the destruction of the original coal structure involves a large amount of energy and processing can be very expensive in terms of thermal efficiency.

2.4 Direct Liquefaction

Direct liquefaction has advantages over the other processes discussed here, in terms of both thermal efficiency and economics. Both of these advantages are derived from the fact that fewer chemical changes are required to convert solid coal into liquids than into gases, and the process conditions are milder. Like gasification, this scheme also involves addition of hydrogen as the method of increasing the hydrogen/carbon ratio. This scheme consists of two alternate processes: (1) hydrogen-donor solvent extraction or dissolution and (2) catalytic hydrogenation.

The first approach is illustrated as the top processes in Figure 2.2. The first process is basically a reaction with a hydrogen donating solvent, and the degree of hydrogenation is relatively low. The purpose of solvent extraction is to produce, with minimum treatment, a relatively clean burning fuel from coal. The fuel can be either in solid form, known as solvent refined coal (SRC), or in liquid form. Hydrogenation not only increases the hydrogen content in coal, but also reduces the undesirable heteroatoms, such as sulfur, nitrogen, and oxygen, by combining them with hydrogen. The degree of removal of these undesirable elements depends on the degree of hydrogenation. In general, in solvent refined coal all the inorganic sulfur and part of the organic sulfur are removed, and the sulfur content is reduced to below 1 %. Two important factors in solvent extraction are the nature of the donor solvent and the presence of hydrogen pressure. To increase the hydrogen donor capability the solvent is frequently hydrogenated before use. In commercial practice the solvent is obtained by recycling part of the oil product stream. In the present research, this approach was followed to convert coal into a solid carbon product (pitch) instead of a liquid fuel. Also the effectiveness of the process-generated recycle solvents was investigated as hydrogen donor solvents without a separate rehydrogenation step, which is typically employed in the catalytic hydrogenation process. Here there is either a separate catalytic step of solvent hydrogenation or there is addition of catalyst during the liquefaction reaction.

When catalyst is added to the coal-solvent slurry, the process is known as direct catalytic hydrogenation, or hydroliquefaction. This process is represented by the second process in Figure 2.2. Catalysts such as cobalt molybdate, tungsten, molybdenum sulfide, and iron oxide have been successfully used. The operating conditions are approximately

450^{o} C and 2000-4000 psia hot hydrogen pressure. The degree of hydrogenation is much higher than that obtained with solvent extraction, and thus the problem of solid separation is much less severe due to enhanced conversion. Furthermore, most of the heteroatoms in coal are converted to H_2S, H_2O, and NH_3. These compounds leave with the gas stream, resulting in a much cleaner product than solvent-refined coal. The coal is converted to liquids ranging from heavy to light oils and gases.

The subsequent discussion of direct liquefaction will only include the hydrogen-donor solvent extraction process and is the focus of the remainder of this chapter.

2.5 Coal Liquefaction Parameters

In this section some of the different factors that affect the ability of coal to be processed by direct coal liquefaction will be discussed. These include the coal composition, the type of solvent, either pure or coal-derived, the mineral matter in the coal, the presence of a hydrogen atmosphere and the temperature of the hydrotreatment reaction.

2.5.1 Coal Composition

Coal rank affects the process of liquefaction. This relationship has been extensively studied in the past with varying results. One reason for such discrepancies is the fact that the same rank of coal could be very different in composition according to the geographical region in which it originated and the petrographic composition of the coal.

Fisher et al. [6] investigated the influence of coal rank on coal conversion while considering the effects of petrographic composition. They found that coals with more

than 89% carbon content are unsuitable for hydrogenation and give a low liquid yield (liquid products). High volatile bituminous coals are the best for liquefaction, and low rank coals such as lignite and sub bituminous gave lower liquid yields as well. Also, the low rank coals are more sensitive to reaction temperature and pressure. The results of this study can be seen in Figure 2.3.

Neavel [12] found that coal conversion to benzene solubles (asphaltenes and lighter hydrocarbons) decreased as coal rank increased. This experiment was performed using hydrogenated creosote oil as the hydrogen donor solvent at approximately 400 °C. Neavel's results are shown in Figure 2.4.

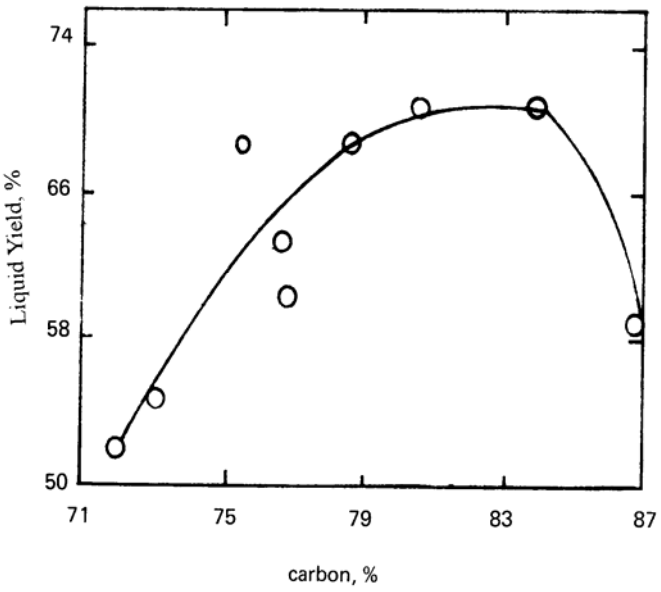


Figure 2.3 Effect of carbon content on liquid product yield [6]

2.5.2 Liquefaction Solvents

The composition of the liquefaction solvent can have an enormous effect on the products of direct coal liquefaction. It affects overall conversion, amount of hydrogen consumed, the degree and quantity of retrograde reactions, and the quality of liquid products [8]. The process of liquefaction thermally decomposes the macromolecules of coal into smaller, free radical units. At this point, if hydrogen is added, the free radicals will be stabilized and the small molecules will become stable and soluble. The liquefaction solvent is chosen such that it has hydrogen donation capability, so that the most efficient transfer of hydrogen to these free radicals can be achieved.

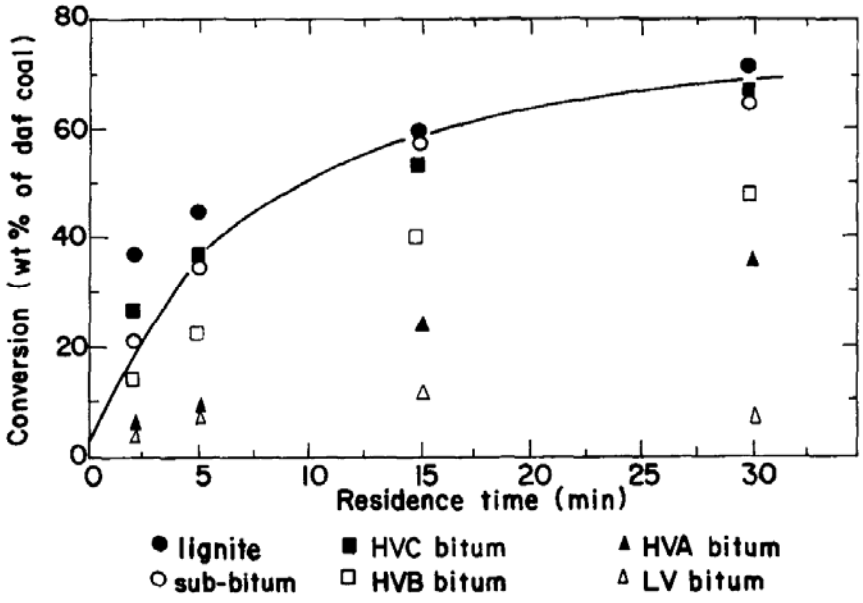


Figure 2.4 Variation in the yield of benzene solubles with rank and reaction time[12]

Four different types of solvents based on their effects on coal were defined by Oele et al. [13]: non-specific solvents, specific solvents, degrading solvents, and reactive solvents. Of these four types, only specific and reactive solvents are of interest to direct liquefaction. Specific solvents dissolve 20-40% of the original coal at temperatures about or below 200° C. Some of these solvents are electron donors and the process is a physical dissolution. Some solvents that fall into this group are N-methylpyrolidone (NMP) and pyridine. A reactive solvent actually undergoes a chemical reaction with the species that is being dissolved. This is the common type of solvent used in high temperature direct liquefaction reactions. The solvent reacts with coal by donating hydrogen to the free radicals that are formed. Tetralin is one such solvent.

Liquefaction experiments were performed by Orchin and Storch [14] in order to determine the ability of several reactive solvents to convert coal to benzene solubles. These reactions were carried out at 400 °C under a hydrogen atmosphere. The results are shown in Table 2.4. The least effective solvent is a high boiling aromatic compound or a hydroaromatic compound that dehydrogenates slowly at the reaction temperature and low pressure. The most effective solvents contained an aromatic hydroxyl group as well as a hydroaromatic ring.

2.5.3 Composition of Recycle Solvents

Industrial processes involving coal-derived solvents as liquefaction solvents always isolate process-derived recovered solvents, which can be recycled back to the process, thereby minimizing the addition of fresh solvent. The chemical composition of these recycle solvents controls the overall behavior of the coal liquefaction process.

Each class of chemical compounds found in industrial recycle solvents has been shown to have relative merits. The components to be considered include H-donors, H-shuttlers and H-abstractors. They have influence on the rate and extent of coal dissolution, coal conversion, hydrogen consumption, product distribution, and the ability to regenerate solvents. In the SRC process (schematic shown in Figure 2.5) no commercial catalyst is employed and only the intrinsic mineral matter entering with the coal acts as a catalyst for coal liquid upgrading and/or maintenance of proper solvent quality. So, in a way, the SRC process resembles the work undertaken in this research, the only difference being it was continuous. An external catalyst is not necessary for dissolution, since the coal is often substantially dissolved through interaction with the solvent by the time the coal exits the reactor. The nature of the process and the selectivity to the various products are primarily governed by the composition of the recycle solvent.

Table 2.4 Effectiveness of some typical solvents for hydrogenation [14]

Solvent	**Benzene Soluble(%, maf coal basis)**
o-Cyclohexylphenol	81.6
1,2,3,4-Tetrahydro-5-hydroxynaphthalene	85.3
Tetralin	49.4
Cresol	32.1
Dicyclohexyl	27.2
Naphthalene	22.2
o-Phenylphenol	19.6

[a] With 1 atm cold hydrogen pressure without catalyst. The reaction time is 0.5 hr at 400°C with a 4:1 solvent/coal ratio.

Coal conversion can be envisioned to occur in three stages: solubility of the coal, defunctionalization of the coal and hydrogen-transfer, and rehydrogenation of the solvent. In each of these stages, the nature of the solvent can affect the rates of reaction and the distribution of the products. In the dissolution stage, because of high temperature, the highly crosslinked structure of coal fragments into radicals, which in the presence of H-donors are capped into stable species. In the absence of hydrogen-donor solvents, the original radicals or the smaller soluble species may recondense to form char or coke. The solvent governs product selectivity by controlling the path taken by the intermediate radicals. When a bond cleaves, at least three different pathways are available for product formation: H-abstraction, rearrangement and elimination, and addition to aromatics. The availability of H-donors will determine the preferred path. The specific chemical properties of interest in recycle solvents are:

1) Hydrogen-donor capacity of the solvent – hydrogen donors are believed to be important in the defunctionlization of the dissolved coal and the prevention of char formation. The principle sources of hydrogen appear to be partially hydrogenated aromatic hydrocarbons: tetralin and its homologs, partially hydrogenated pyrene, phenanthrene, and other polycyclic aromatic compounds.
2) Physical solubilization of coal products – effective solvents for coal solubilization must contain polar compounds. Assuming the concept of specific solubility parameters applies, then the good solvents should contain such components as polyaromatics, phenols, pyridines, aromatic ethers, and quinolines and their derivatives.

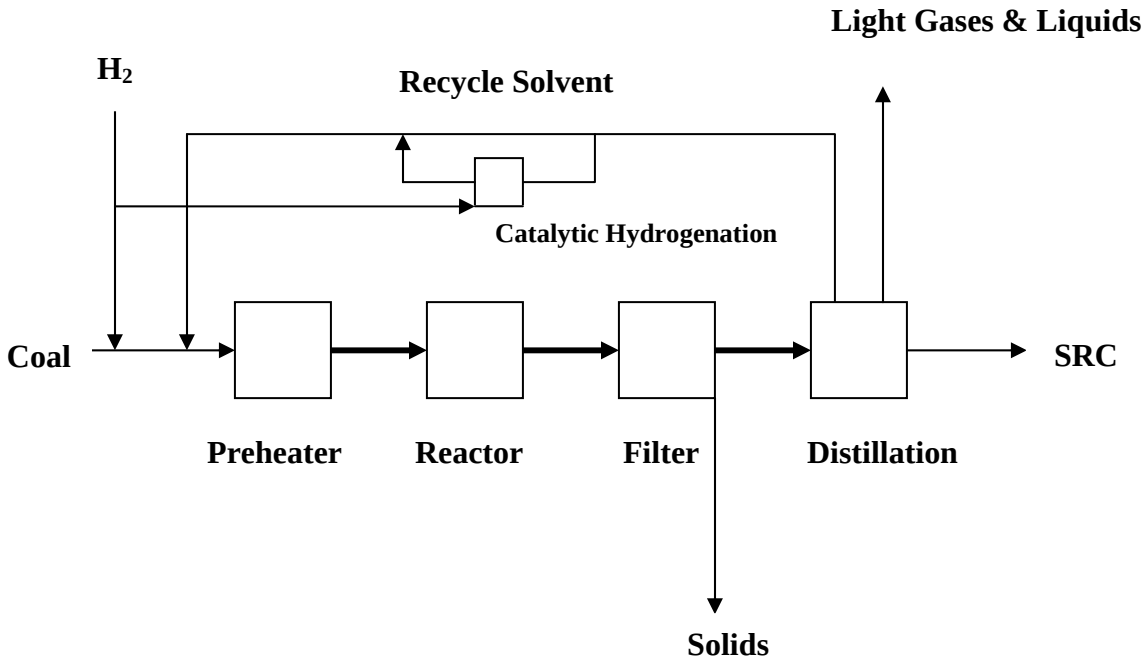


Figure 2.5 Schematic sketch of the typical SRC process used industrially [22]

3) Hydrogen transfer capability (H-shuttling) – hydrogen transfer is another mechanism for dissolving coal, whereby hydrogen may be supplied from the coal itself or from the SRC to cap off radicals and form smaller soluble species. Reports by Neavel [27] indicate that naphthalene can dissolve 80 % of a vitrinite-rich bituminous coal at short contact times and at temperatures over 750 ^{o}F. It was proposed that this dissolution was the result of the shuttling of hydrogen from one position in the coal to another. Naphthalene acts as an H-acceptor and the resultant free radical formed by the addition of an H-atom act as an H-donor. A reaction of this type is even more probable for phenanthrene or pyrene since they are better H-acceptors than

naphthalene. The structures which can contribute to good shuttling properties within recycle solvents are: Naphthalene and its alkyl derivatives, phenanthrene and its alkyl derivatives, heterocyclic polyaromatics etc. This effect is explained in more detail in the later section.

4) Chemical structures associated with char formation – recycle solvents may contain compounds which are prone to or which can promote char formation. Heavy phenols and highly aromatic compounds are some of these compounds [22].

2.5.4 The Effect of Polyaromatic Hydrocarbons (H-Shuttlers)

Although H-donors are the major controlling species in coal liquefaction, they are not the sole controlling factor. Several workers have reported [28, 29, 30, 31] that coal or SRC can produce significant amounts of hydrogen in liquefaction processes. In fact, it has been reported [30,31] that at relatively short reaction times and in the presence of a polyaromatic non-donor solvent, over 80 % of the reactive macerals of coal (vitrinite) can be converted to a pyridine soluble form in the absence of hydrogen gas or a hydroaromatic. The polyaromatic non-donor solvent (e.g. naphthalene) aids in the redistribution of hydrogen among different coal species. This phenomenon was termed H-shuttling. A few possible mechanisms by which shuttling may occur are shown in Figures 2.6. These mechanisms show that on heating coal to liquefaction temperatures, high concentrations of free radicals are formed by thermal bond breakage. If conventional hydroaromatic H-donors are present, the radicals are stabilized by hydrogen transfer from the solvent. If no hydrogen donors are present, the radicals must stabilize in other ways (e.g. by recombination, aromatic ring alkylation, or H-abstraction from the coal itself).

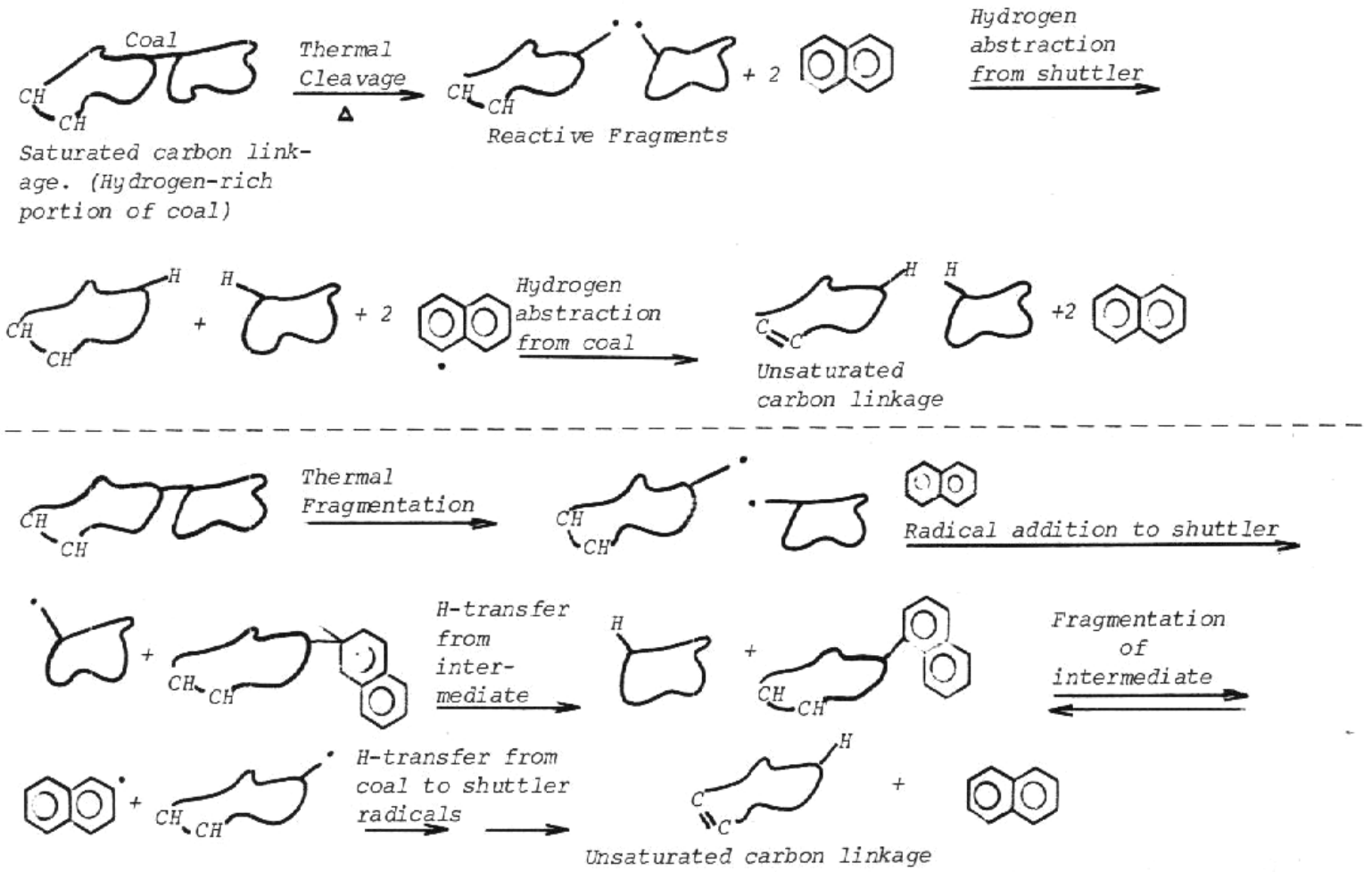


Figure 2.6 Possible mechanisms of hydrogen shuttling [22]

H-shuttlers can aid in this stabilization.

In such a sequence no net change would occur in the shuttler or the H/C ratio of the coal; however, the content of unsaturated carbons in the coal products would increase. A number of authors have reported on the ability of non-donor polyaromatic solvents to dissolve bituminous coals [28]. Coal dissolution by these solvents is generally associated with major hydrogen exchange reactions between the coal and the solvent. The extent of H-exchange by phenanthrene with coal at close to liquefaction conditions (662 ^{o}F, long times) was measured using deuterium, tritium, and ^{14}C tracers[32]. This work showed that 9-15 % of the hydrogen of the coal exchanged and 80 % of the coal dissolved. H-donors and H-shuttlers can work together synergistically when the content of H-donors is limited in the solvent. In solvents of limited but measurable H-donor concentrations, correlations exist between the content of polyaromatic ring compounds and the extent of coal conversion. This is shown in Figure 2.7 for a series of coal-derived solvents with low H-donor capacities. In summary, hydrogen donation by SRC, coal or residue can be aided by the action of H-shuttlers which can transfer hydrogen from one portion of the coal to another. The most efficient H-shuttlers appear to be higher molecular weight, more highly condensed, aromatic hydrocarbons.

2.5.5 Mineral Matter in Coal

Many scientists have reported the benefits of intrinsic mineral matter for catalyzing coal conversion reactions. Most of the catalytic activity has been ascribed to the presence of pyrite (FeS_2) or the reduced form of pyrite, pyrrhotite [22].

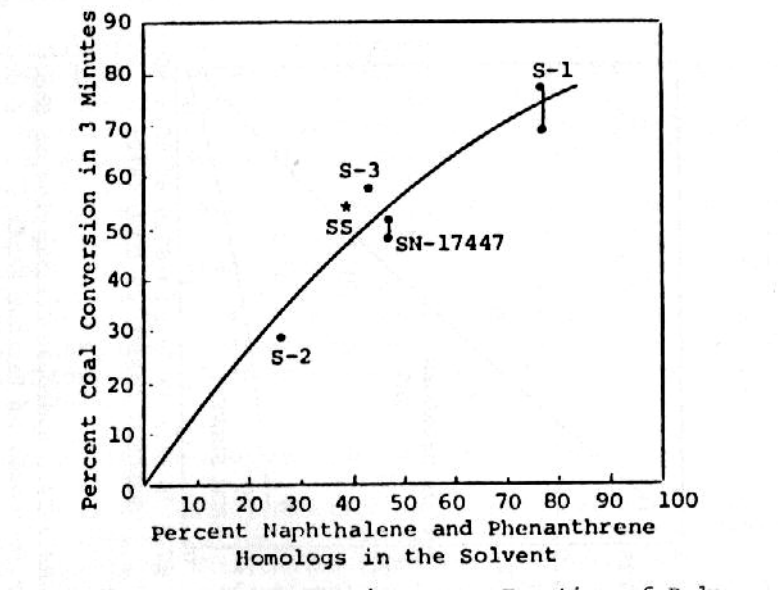


Figure 2.7 Effect of polyaromatic hydrocarbons on coal conversion [22]

Relatively little work, however, has been done on the mechanisms of the possible synergism of acid and metal activity, or on the relationship of such synergism to solvent rehydrogenation.

In a recent study [11] on the hydrogenation of a high-vitrinite Indian coal (North Assam) in the absence of a solvent, the catalytic effect of mineral matter was studied by characterizing the coal ash and by adding specific minerals. The best correlation to activity was found using (organic plus pyritic) sulfur. Other materials - iron, titanium and kaolinite (the prevalent clay) - also correlated with coal conversion to benzene- soluble products. Iron pyrite was suspected to be the active form of iron but conversion also increased with the addition of sulfur or titanium hydroxide.

In another study Whitehurst et al. [22] proved that pyrite addition increased the pyridine solubility of four German coals. Samples of a coal enriched in mineral matter were more extensively converted. These reactions were carried out in methyl naphthalene at 752 ^{o}F under 3000 psi of hydrogen for 2 hours. These studies indicate the effect of iron pyrite on the solvent-solvent interactions that occur during the liquefaction of coal. These results showed that the rate of solvent-solvent hydrogen transfer reactions occurred at a higher rate in the presence of coal containing pyrite than in solvent-solvent reactions alone.

A different approach to study the effect of mineral matter in coal is to selectively remove the mineral matter content without altering the organic composition of the coal before reaction [22]. The mineral matter present in coal can be selectively removed depending on the type of pretreatment. After the pretreatment of these coals to remove the ash content, the coal conversion dropped with lower ash content (see Figure 2.8) and the hydrogen consumption dropped with lower ash content signifying that some catalytic activity can be attributed to the presence of pyrite [22]. The coal in this study was Wyodak-Anderson coal containing relatively little pyrite but catalysis of hydrogen gas reactions did respond to total ash content. Such behavior would indicate that even ion-exchangeable iron may have catalytic properties.

In summary there are clearly effects of coal mineral matter on the progress of liquefaction. Mineral matter catalyzed hydrogen gas consumption and other reactions of coal and its products. It also aids in solvent rehydrogenation but its activity is low. Acid demineralization, especially for subbituminous coal, increases coal reactivity but

decreases conversions and SRC yields at long coal conversion times because of increases in both regressive and forward reactions.

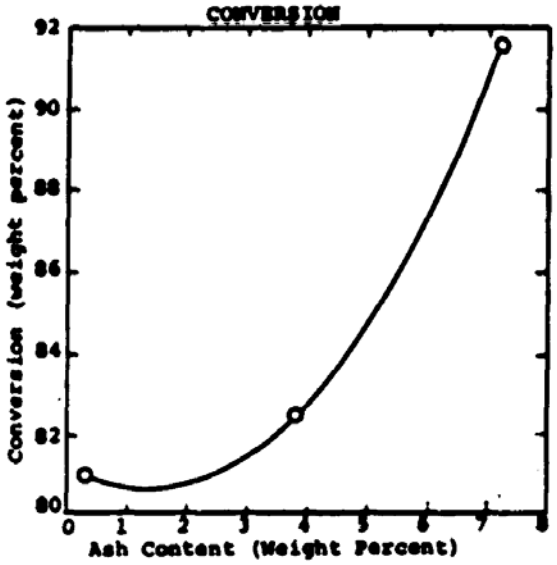


Figure 2.8 Wyodak coal conversion vs. ash content [22]

2.7.6 Hydrogen Pressure

The presence of a hydrogen atmosphere can greatly benefit the production of soluble coal increasing the product yield. Molecular hydrogen at high pressure could donate hydrogen and stabilize the coal free radicals in one of two ways: (1) directly donate hydrogen to the free radical or (2) transfer hydrogen to the donor solvent, which can then be transferred to the coal particle. Yen et al. [26] showed that when tetralin is used as a donor solvent, the yield of benzene insolubles under a nitrogen atmosphere was 25.3%. When the atmosphere was changed to hydrogen, the yield of benzene insolubles

decreased to 13.8% indicating more conversion to benzene solubles. Tomic and Schobert [19] also observed an increase in the amount of conversion when a hydrogen atmosphere is used instead of an inert atmosphere during liquefaction without solvents or catalysts. This increase in conversion is believed to occur as hydrogen reduced the amount of retrograde reactions at high temperature.

There also has been some work on the exact source of the hydrogen during the liquefaction reactions. This hydrogen can come from a variety of sources: the solvent, gaseous hydrogen, or from the coal itself. The most efficient source is the hydroaromatics in the solvent but if such materials are limited in concentration, hydrogen gas or coal become the dominant sources. Whitehurst et. al. [22] have shown that even at short times hydrogen gas can be the dominant source of hydrogen for low rank coals where the demand for hydrogen is largest.

These liquefaction reactions are also sensitive to H-donors, hydrogen gas and H-shuttlers. The rate of coal dissolution is proportional to the concentration of hydroaromatics in synthetic recycle solvents. Whitehurst et al. [22] found the conversion of Illinois #6 coal at 3 minutes in a series of solvents with varying tetralin concentrations increases with the tetralin content in the solvent. This simple relationship is somewhat complicated by hydrogen donation from other sources such as hydrogen gas or the coal itself. It has been proved that low rank coals can give increased yields at short times by application of hydrogen pressure. For higher rank coals (bituminous) hydrogen donation from gas phase is small [22]. It is suggested that bituminous coals are efficient sources of hydrogen because a high proportion of the mass is plastic or mobile at liquefaction temperatures.

The donation of hydrogen from hydroaromatic structures in coal can be assisted by certain highly condensed aromatic molecules in the solvent. Such molecules are not net donors of hydrogen but can rapidly equilibrate with hydroaromatics in the coal and can thus “shuttle” hydrogen from one region of the coal to another. Figure 2.7 shows a group of solvents of limited H-donor capacity, containing naphthalene and phenanthrene homologs, where the amount of coal becoming soluble in 4 minutes is proportional to the concentration of polycondensed aromatic compounds in the solvent [22]. It is noteworthy that a good shuttling solvent can even induce higher solubility than a solvent containing 40 % tetralin (SS in Figure 2.7). So, bituminous coals can give the highest yields and require little hydrogen, but the presence of either good hydrogen donors or hydrogen shuttlers is necessary for high conversion. Sub-bituminuos or lower rank coals can give high yields of soluble material but at a slower rate.

2.5.7 Temperature

Increasing the temperature of the reaction during coal liquefaction increases all reaction rates. This includes rates of coal dissolution, heteroatom rejection, hydrogen consumption, gas formation and charring [22]. The effects of increasing temperature on conversion for bituminous coals have been found to be small at short contact times. With subbituminuos coals, for which the rates of dissolution are considerably slower than for bituminous coals, raising the temperature may be desirable for dissolving coal. With one subbituminous coal (Wyodak Anderson) increasing the temperature to 820, 840, 850, and 860 ^{o}F gave increasing conversion at short times. The net effect of increasing the temperature of reaction in long contact time coal conversion is to decrease the SRC yield

and increase the yield of light hydrocarbons. This is true either with or without hydrogen donors in the solvent. The products of high temperature conversion also contain lower concentrations of highly polar fractions and are therefore more soluble in hydrocarbons, which is why even though the SRC yield might decrease, the overall conversion is increased due to good solubility of the SRC and the increased light hydrocarbons content in the extracting hydrocarbons.

2.6 Mechanisms of Liquefaction

It is proposed that the transfer of hydrogen to coal from a solvent follows a free radical mechanism, in which the coal molecules are thermally cleaved into free radicals, which seek stabilization [21]. Wiser [24] concluded that during each of these ruptures of the covalent bonds, two free radicals are formed, and that these free radicals are capped in one of three ways: (1) addition of atoms (such as hydrogen) or other radical groups to the free radicals, (2) rearrangement of atoms within the free radical, and (3) polymerization of the free radical.

The first method of capping the free radical is the desired method when performing coal liquefaction with a hydrogen donor solvent. This allows the large coal molecules to be thermally degraded, capped with hydrogen, and stabilized as low molecular weight, more soluble and hydrogen-rich species [22]. The second and third methods take place when there is not a hydrogen donor solvent available or the hydrogen donor components in the solvent are limited. If the free radical species or the reacting solvent contains polyaromatic units (H-shuttlers), the free radical species could cap themselves, by shuttling hydrogen from the hydrogen rich part of the coal. Finally, if the

free radical species is stable and in the presence of other free radical species, polymerization or retrograde reactions could take place. This is the basis for the formation of coke, char, and other large molecular weight, insoluble species. Therefore, for the formation of low molecular-weight carbon-product precursors, the first method is preferred.

The conversion of coal to liquid hydrocarbons can be visualized as a progressive hydrogenation through a series of intermediate products as preasphaltenes, asphaltenes through oils (carbenes and carboids). However, Berkowitz [33] illustrates, as shown in Figure 2.9, what is believed to be the general process occurring during donor-solvent liquefaction. The intermediate stabilized species are the preasphaltenes, which are further reduced in molecular weight to asphaltenes and then to distillable oils and hydrocarbon gases. The latter compounds are also generated at each step of the main reaction path as by-products. The first step in this reaction path is coal solubilization or autostabilization, which involves mostly redistribution of hydrogen within the coal matrix, with the solvent acting as a net shuttler of hydrogen [12]. The second step occurs when secondary hydrogenation takes place. Secondary hydrogenation depends on the specific reaction conditions and drives the products toward lower molecular weight species.

Most of the information obtained concerning the chemistry and kinetics of coal liquefaction has been determined from reactions with coal and a model hydrogen donor such as tetralin. One hypothesis for the reaction of coal and tetralin is illustrated in the scheme below in Equation 2.1. This reaction gives a way to correlate the solubilization

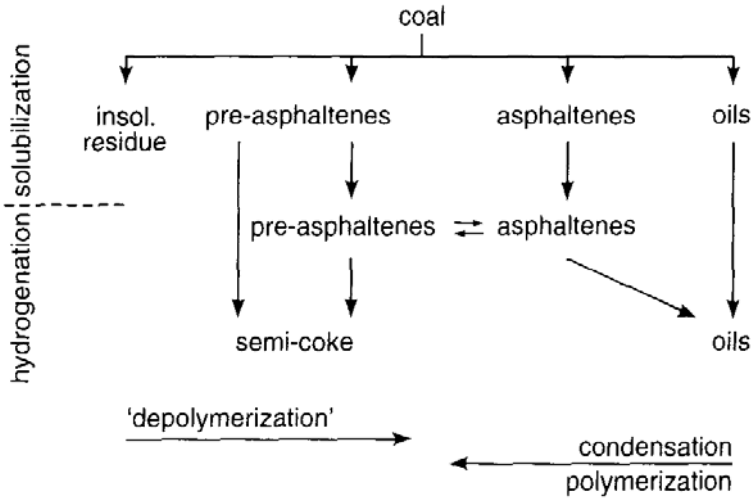


Figure 2.9 Conceptual reaction sequences in coal liquefaction [33]

of the coal via hydrogen transfer by quantifying the conversion of tetralin to naphthalene at varying reaction conditions [12]. However, this is not the only possible reason for the formation of naphthalene from tetralin. The tetralin could undergo dehydrogenation that results in the formation of hydrogen gas. Alternately tetralin could be converted by isomerization to methyl indane as well as hydrogen donation to form naphthalene [4].

$$\text{Coal} + \text{Tetralin} \longrightarrow \text{Coal-derived products} + \text{Naphthalene} \qquad 2.1$$

Through laboratory studies and pilot plant operations, properties of coal that affect liquefaction results have been compiled and are summarized in Table 2.5

Table 2.5 Fundamental properties important in coal liquefaction [33]

Property	Influence	Desired level
Rank	Liquids yield	Medium
Ash content	Operations and handling	Low
Moisture content	Thermal efficiency	Low
Hydrogen content	Liquids yield and hydrogen	High
Oxygen content	Gas make and hydrogen	Low
Extractability	Liquids yield and quality	High
Aliphatic character	Liquids yield and quality	High
Reactive macerals[a]	Liquids yield	High
Particle size	Operations	Fine/very fine

[a] Principally vitrinites and exinites

2.7 Liquefaction Processes

Commercial liquefaction technologies involve hydrogenating coal in a solvent slurry under elevated temperatures and hydrogen pressures (370-480 ^{o}C and 1500-4000 psig). High temperatures are required to crack the coal thermally and produce reactive fragments while high hydrogen pressures are required to cap these sites with hydrogen. Depending on the reaction conditions lower molecular weight gases and liquids are formed and recovered from the remaining solid material. Three main commercial liquefaction technologies are discussed below.

2.7.1 H-Coal Process

The H-Coal process was developed by Hydrocarbon Research Inc. to convert high-sulfur coal into boiler fuels and synthetic crude oil. This process utilized a catalytic ebullated-bed reactor, in which the reaction mixture is recycled upward through the reactor to maintain the catalyst in a fluidized state. The process used crushed (60 mesh)

coal slurried with recycled oil, pressurized to 3000 psig and mixed with compressed hydrogen. The mixture was then preheated and fed to the ebullated-bed catalytic reactor that operated between 340-370 ^{o}C. The gas product after separation into light hydrocarbons, ammonia and hydrogen sulfide, is mostly hydrogen, which is recompressed and combined with fresh coal-oil slurry. The liquid-solid mixture is separated in a flash separator to recover light and heavy hydrocarbons. The remaining solids and heavy oil are processed in a hydrocyclone and a vacuum distillation column. The process requires between 14000-20000 scf of hydrogen for every ton of coal, depending on the type of oil product desired. A portion of the hydrogen needed is produced in the process itself, while make-up hydrogen is required. The conversion of coal to liquid and gas products for this process is about 90 %.

2.7.2 Solvent Refined Coal (SRC) Process.

The SRC process is a non-catalytic process that converts high ash and high sulfur coal into gas, liquid, and/or solid fuels. The product from the process is a solid, carbonaceous material that contains less than 1 % sulfur and 0.2 % ash. Pulverized coal mixed with process-derived solvent combines with gaseous hydrogen at 425-455 ^{o}C and 1030 psig. The product gases are processed to recover hydrogen which is recycled to the process. The slurry from the separator is processed in a filtration unit to recover a high molecular weight solvent which is then recycled and mixed with fresh raw coal. As mentioned earlier this principle of the SRC is used in the current research to study the process-derived solvent as a hydrogen donor. The final solid product contains very low amounts of sulfur and ash. The schematic of the process is shown in Figure 2.5.

2.7.3 Exxon Donor Solvent (EDS) Process

The EDS process was developed by Exxon to produce liquid products from a wide range of coals. Like SRC this too is a non-catalytic process based on the solvent recycle principle, the only difference being employment of a separate solvent rehydrogenation step before recycle. Crushed coal is slurried with recycled donor solvent and mixed with recycled hydrogen at 425-465 ^{o}C and 1500-2000 psig. The products are separated into three fractions: light hydrocarbons, a naphtha fraction and heavy distillate. The heavy distillate is processed in a vacuum distillation column to yield jet fuel and heating oil. A portion of the heavy distillate between 205-455 ^{o}C boiling range is hydrotreated and recycled to form the slurry feed with fresh coal. The remaining bottoms product can be converted to heavy oil using a process called flexicoking. One of the unique features of the EDS process is the ability to adjust the recycled hydrogen donor solvent based on the characteristics of the raw coal feed. The quality of the solvent can be adjusted by controlling the reaction in the hydrotreatment step. By tailoring the donor solvent to match the feed coal, the liquid products can be optimized.

2.8 Carbon Products from Coal

The most common use of coal or products from coal is production of electricity by combustion. In the future, due to strict environmental regulations, this usage of coal may be limited. The ongoing research in developing non-fuel uses of coal will become significantly important. This includes use of coal as a feedstock for the production of electrodes, artificial graphite, carbon fibers, carbon foams, activated carbon, carbon blacks, etc. The building block of these products is generally graphite. Graphite is a form

of carbon in which carbon atoms are in the sp^2 hybridization state and trigonally bonded in planar sheets. The planes are normally stacked in the hexagonal ABAB sequence, although the rhombohedral ABCABC stacking is also encountered. Figure 2.10 shows the crystal forms of graphite.

Graphite in its ideal form would have no defects in the arrangement of its layers of carbon atoms and is hence highly anisotropic. The deviation from the ideal graphitic structure gives rise to variations in properties like thermal conductivity, electrical conductivity, coefficient of thermal expansion, hardness, porosity, etc. and hence a variety of different carbon products are possible. The following sections summarize some of the carbon products which have the potential of being made from coal.

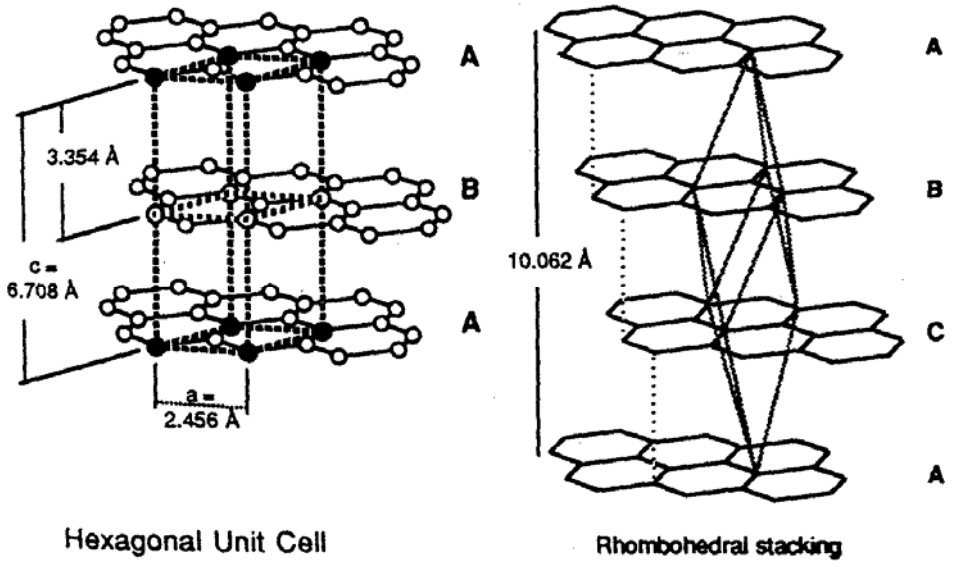


Figure 2.10 Crystal forms of graphite [2]

2.8.1 Pitch

Pitch is a complex mixture of polycyclic aromatic hydrocarbons. It can be a feedstock for the production of two to four ring aromatic chemicals. Currently, the majority of coal-based pitches are derived as by-products from the production of metallurgical coke in the coke ovens. The volatiles from the coking process are captured and condensed to get coal tar. This coal tar can be further separated into different products like tar acids, tar bases, oils and a solid residue known as coal-tar pitch. However the environmental regulations placed on the existing coke ovens and the decline of the U.S. steel industry places doubts on the future supply of coal tar pitch. Thus an alternate and environmentally friendly route of producing coal-derived pitches is required. The solvent extraction of coal combined with hydrotreatment can form one such route.

Pitches can also be made from petroleum. Petroleum pitch is a by-product obtained from the catalytic cracking process. Petroleum pitch can be produced from these heavy residues by thermal treatment, vacuum or steam stripping, oxidation, or distillation. The types of pitch that are produced depend on the treatment of the residues. Usually, longer treatment times and higher treatment temperatures result in a more aromatic pitch with an anisotropic texture.

Another type of pitch that can be formed is mesophase pitch. This pitch exists in a state where the macromolecular components exhibit an ordered anisotropic liquid crystalline structure. These pitches are highly oriented. Mesophase pitches can form when isotropic pitch is heated above 350 °C. After melting, the pitch undergoes dehydrogenative condensation to increase the pitch aromaticity. The increase in

aromaticity produces larger, more planar molecules, which come together to form tiny anisotropic spheres of liquid crystalline-like material. As these spheres collide, they coalesce to form larger spheres until the pitch becomes 100% bulk mesophase. Such a pitch can be used to produce high strength carbon fibers.

The end use of a pitch is determined by its physical and chemical properties. Pitch can be used as a binder in the production of anodes and electrodes to hold coke particles together. This type of pitch needs to have a high-carbon yield and cannot affect the properties of the finished product. Pitch can also be used to reduce the porosity of carbon products where high density and strength are required. This type of impregnation pitch should have a low viscosity and low ash content. The production of carbon fibers is another possible use for pitch. This pitch requires low solids content, a moderate softening point for ease of spinning, and high reactivity toward stabilization.

2.8.2 Coke

Metallurgical coke is produced by high-temperature carbonization of coal. This is done by heating the coal in the absence of air to produce a solid carbon residue. The solid residue is metallurgical coke and is used to produce iron from iron ore in a blast furnace.

Petroleum coke is produced from the heavy fractions of crude oil which are formed during petroleum processing, by the most common process known as delayed coking. High-grade petroleum coke is used by the aluminum industry to extract aluminum from aluminum oxide ore. Petroleum coke can also be used to produce graphite electrodes and some carbon-carbon composites.

The properties of coke determine its end use. Optical texture is one such important property which characterizes the degree of anisotropy of a coke. The anisotropic cokes have large crystalline domains while the isotropic cokes have a fine-grained structure as shown in Figure 2.11. It has been found that isotropic coke can be obtained by coking the extract obtained by the solvent extraction of raw coal; on the other hand, coke obtained from the extract of hydrogenated coal shows large anisotropic domains.

Isotropic coke is suitable for the production of isotropic graphite, which is used as a core material for high-temperature gas-cooled nuclear reactors. Anisotropic thermal expansion in the core material creates large internal stresses making the reactor operation unsafe. Hence the core material must have isotropic properties. On the other hand, electrodes for the steel industry are made from graphite which is obtained from anisotropic coke. Such electrodes are capable of conducting a large amount of electric current at elevated temperatures and hence rely on the well-oriented anisotropic structure.

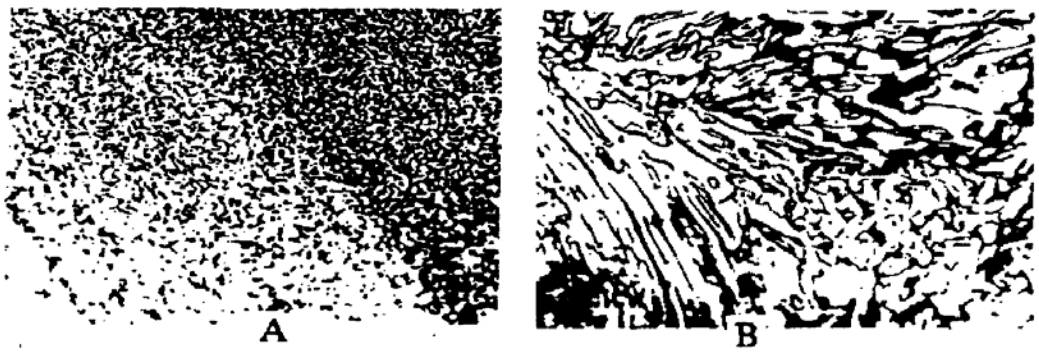


Figure 2.11 Optical structure of cokes A: isotropic coke B: anisotropic coke

2.8.3 Carbon Fibers

Carbon fibers can be produced from coal-derived or petroleum-derived pitches, as well as organic and synthetic polymers. They are generally used as reinforcement in composite materials. A carbon-carbon composite consists of carbon fiber reinforcement bound together by some form of matrix material. These materials are suitable for aerospace applications due to their high strength-to-weight ratio, high-temperature strength and low coefficient of thermal expansion. Activated microporous carbon fibers can be used as adsorbents for gases and liquids or for gas storage. Other uses include membranes, specialty fabrics, biomedical devices, etc. Mesophase pitch fibers can be tailor made based on the mesophase content of the precursor pitch to produce fibers of differential modulus and strength.

2.8.4 Carbon Foams

Carbon foams can be produced from a variety of carbon sources including bituminous coals. Some foam is made from raw coal directly. The coking of raw or hydrogenated coal under controlled conditions of temperature and pressure causes controlled expansion (swelling) and results in the formation of carbon foam which in some cases can be subsequently graphitized. Carbon foams are light-weight materials and their properties can be tailored through the selection of appropriate bituminous coal precursor, foaming conditions and heat treatment conditions. Carbon foams have been made from raw coal, coal extracts, mesophase pitches from petroleum and naphthalene. Calcined carbon foams with low thermal conductivity can be used to provide thermal insulation. On the other hand, graphitized carbon foams with high thermal conductivity

have applications in thermal transfer systems like heat exchangers. Heat-treating at a higher temperature increases graphitic ordering and foams with high electrical and thermal conductivity and high elastic modulus can be obtained. The carbon foams can also be infiltrated with polymers or metals to form composite materials.

2.8 WVU Coal Extraction/Hydrotreatment Work

Solvent extraction of coals to produce low-ash extract material was studied at WVU using standard pure solvents. The extraction solvents tested were dimethylformamide(DMF), dimethylacetamide(DMAC) and N-methylpyrrolidone (NMP). The extraction efficiency was found to be NMP>DMAC>DMF for the reflux extraction at the normal boiling point of the solvent. While the NMP reflux-extraction of raw coal gave less than 40 % yield, extraction at 350 ^{o}C and elevated pressure gave higher yield (~68 %). Hydrogenated coal gave higher NMP extraction yields (> 70 %) even at room temperature [34].

Relevant work related to hydrotreatment of coal using coal-derived solvents was also done at WVU. In this work different coal-derived solvents were studied for their potential to produce THF soluble species from coal [35]. Three fractions of a middle-distillate by-product liquid from the production of high quality char, along with heavy cresote oil and carbon black base were used as H-donor solvents under varying conditions such as gas pressure, gas composition, and solvent-to-coal ratio. The coal-alone conversion was found to increase with initial gas pressure in the reactor and also with use of hydrogen instead of argon in the gas phase. This suggested that gaseous hydrogen played an important role in producing soluble species from coal. The important

finding was that the coal-alone conversion did not show any dependence on the solvent-to-coal ratio in the hydrogenation reactions. This suggested that a lesser amount of solvent could be used to achieve the same conversion. The coke yield of the coal-derived pitch depended linearly on the pitch softening point but showed no dependence on the reaction conditions like pressure, gas composition, solvent-to-coal ratio or the hydrogenation solvent. The work also showed that the elemental composition of the recycle solvent is similar to that of the original solvent, thus giving a process generating its own process solvent, minimizing the need of make-up solvent.

CHAPTER 3

EXPERIMENTAL

This chapter gives details on all of the materials and equipment used in the hydrotreatment/extraction experiments, along with the steps for performing the hydrogenation reactions, extracting and separating the products, and testing the final products.

3.1 Materials

Several chemicals and gases used during the course of these experiments along with their supplier and purity are listed below.

Tetrahydrofuran (THF) is used as a solvent during the product separation steps to dissolve the products in order to separate the solubles from the insolubles. THF is obtained from Fisher Scientific and is the histological/optima grade with purity listed as 99% or greater. It is used during all experiments as delivered. Nitrogen and hydrogen are used as the gaseous atmosphere for the hydrogenation experiments. Nitrogen is also used as an inert purge gas during vacuum drying. They are obtained as standard laboratory grade from AirGas of West Virginia.

A high-volatile bituminous coal (Lower War Eagle) is obtained from the southern West Virginia coal fields. A proximate analysis was performed on the coal using Thermo-Cahn's TGA 151 to determine its amount of moisture, fixed carbon, volatile matter, and ash. The results of this analysis along with some other characteristics of

Lower War Eagle are shown in Table 3.1. An ultimate analysis is performed using ThermoQuest's Flash EA-1112 CHNS elemental analyzer to determine the elemental composition of the coal. These results can be seen in Table 3.2. The coal is ground to -20 mesh and dried overnight in a vacuum oven. The vacuum oven is set at 110°C with a nitrogen purge (100 cc/min) and a vacuum of 25 in Hg.

Three coal-derived solvents are tested as hydrogenation solvents. The solvents are named as refined chemical oil (RCO), heavy creosote oil (HCO), and carbon black base (CBB). All the samples are obtained from Koppers Industries, Inc of which the latter two are considered to be similar but from different batches. However, the elemental composition is slightly different for these two Koppers' solvents, and so they are treated as separate solvents. The elemental composition of each raw material is shown in Table 3.2. HCO is a pasty material that needed to be heated in order to process easily. RCO was fluid at ambient temperatures but contained some solid like matter entrained in the fluid. Therefore, it was also heated before processing. CBB was a homogenous liquid at room temperature and so was used as received, but the overall sample was stirred to make it uniform before usage.

Table 3.1 Characteristics of Lower War Eagle coal

Source	Alpha Litwar
County	McDowell County
ASTM rank	hvb
Mean-maximum reflectance of vitrinite	1.09
Total moisture (% wt.)	6.52
Proximate analysis (% wt., dry basis)	
Fixed carbon	63.29
Volatile matter	30.94
Ash	5.77
Petrographic composition (% volume)	
Vitrinite	66.9
Exinite	9.0
Inertinite	24.1

Table 3.2 Elemental compositions[a] of the Lower War Eagle (LWE) coal and the three coal- derived solvents

Elements	**LWE**	**CBB**	**HCO**	**RCO**
C %	88.7	91.6	92.4	91.8
H %	4.68	5.7	5.7	6.9
N %	0.9	0.0	0.7	0.6
S %	0.6	0.5	0.6	0.7
O[b] %	5.12	2.2	0.6	0.0
H/C Atomic Ratio	0.63	0.75	0.74	0.90

[a] Elemental compositions are not on an ash free basis

[b] Determined by difference

3.2 Experimental Procedure for Hydrogenation Reactions

3.2.1 Overview of Hydrogenation Reaction

The conversion efficiency of coal to THF solubles using three coal-derived liquids as hydrogenation solvents in the direct hydrogenation of a high-volatile bituminous coal was investigated. The standard reaction temperature was 400 ºC and the initial cold pressure was 500 psig of hydrogen in the cold reactor. The reaction time of one hour was used for initial experiments to study differences between solvents. These are the standard conditions for the study of reactions between coal and model hydrogen donor solvents. The solvent-to-coal ratio for the present work was 5 to 1. The reason for this high solvent-to-coal ratio, is to maximize the quantity of the recovered process derived solvent available for recycle.

The products of the hydrogenation reactions were extracted using THF in order to determine the overall conversion as THF solubles. The quantity of the coal-derived solvent was included in the conversion calculation for the overall conversion whereas it is excluded for the coal-alone conversion. The extract (THF-soluble fraction) was vacuum distilled to recover a process-derived recycle solvent and a distillation residue. Vacuum distillation is performed to isolate the light fraction (termed “recycle solvent” hereafter). The light distillate is given the name “recycle solvent” because in many similar processes this fraction is recycled to the reactor for further hydrogenation reactions. Hence, testing the effectiveness of the isolated recycle solvents in subsequent hydrogenations was the main scope of this research. The results using fresh and recycle solvent were compared for their conversion yields. The other product, the heavy distillation residue, called pitch, was tested as a possible precursor for carbon-products. A process flow diagram for the

overall experimental procedure is shown in Figure 3.1. Table 3.3 gives an overview of the experiments performed in this research.

Table 3.3 Overall hydrogenation reaction conditions

Run	Trial	Solvent	Temp. (°C)	Atmosphere	Pressure (psig Cold)	Solvent/Coal (wt. %)	Time (hr)
1	A-D	CBB	400	H_2	500	5/1	1
2	A-D	HCO	400	H_2	500	5/1	1
3	A-D	RCO	400	H_2	500	5/1	1
4	A-D	Pass 1 Rec. CBB	400	H_2	500	5/1	1
5	A-D	Pass 1 Rec. HCO	400	H_2	500	5/1	1
6	A-D	Pass 1 Rec. RCO	400	H_2	500	5/1	1
7	A-D	CBB	350	H_2	500	5/1	1
8	A-D	CBB	450	H_2	500	5/1	1
9	A-D	CBB	400	N_2	500	5/1	1
10	A-D	Pass 1 Rec. CBB	350	H_2	500	5/1	1
11	A-D	Pass 1 Rec. CBB	450	H_2	500	5/1	1
12	A-D	Pass 1 Rec. CBB	400	N_2	500	5/1	1

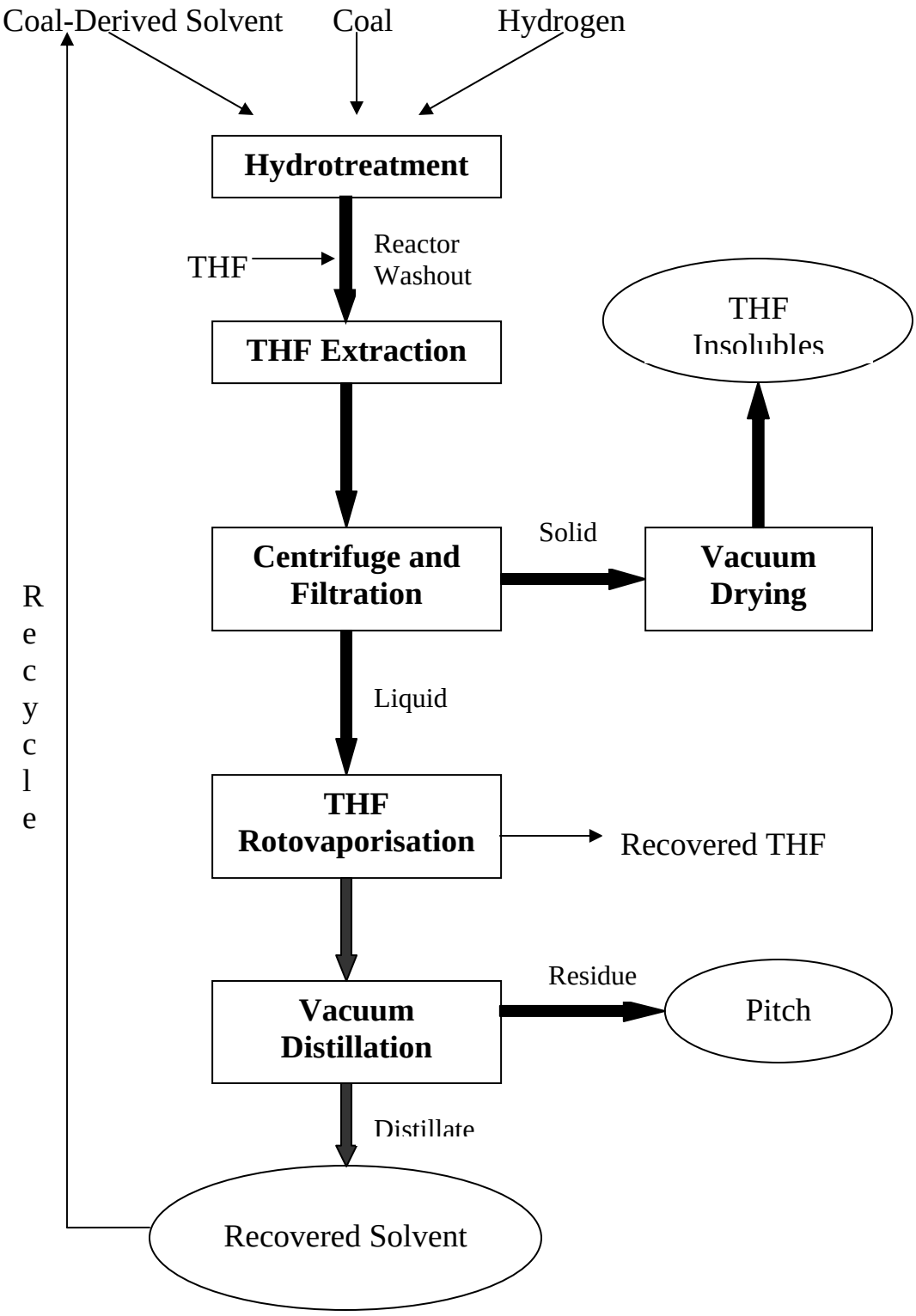


Figure 3.1 Experimental flow sheet for production of carbon product precursors.

3.2.2 Fluidized Sand Bath Preparation

A Techne SBL-2 fluidized sand bath is used to heat the reactors during the coal hydrogenation runs. A TECHNE TL-8D temperature controller regulated the sand bath temperature. The sand bath is filled three-quarters full with a –100 mesh aluminum oxide powder. The sand bath is preheated to a slightly higher temperature usually 20-25 °C above the desired reaction temperature. The extra temperature is required for the rapid loss in temperature that occurs when the cold reactors are immersed into the sand bath. The inlet airflow to the bath is adjusted so that light bubbling of the sand takes place and a uniform temperature is achieved in the bath. A sketch of the overall reactor system is shown in Figure 3.2.

3.2.3 Reactor Preparation

Tubing bomb microreactors (TBMR) made of 316 stainless steel with a capacity of 50 cc. are used for these hydrogenation runs, as shown in Figure 3.3. Usually two tubing bomb reactors are prepared for each hydrogenation run. The reactors are cleaned thoroughly before each use. The inside of the reactor is scoured using a cylindrical wire brush. The threads of the end caps are wiped clean using steel wool. Air is then blown into the reactor stem to remove any particulates from the stem. Once cleaned, one end of the reactor is sealed according to the following procedure. The TBMR was placed in a vise, and a small amount of copper anti-seize lubricant is applied to the threads. The lubricant helps to secure the Swagelok caps and prevents the caps from seizing to the reactor body under the high-temperature reaction conditions. The Swagelok cap is placed

on the reactor and tightened until hand tight. An extra turn is added using a wrench to seal the cap fully.

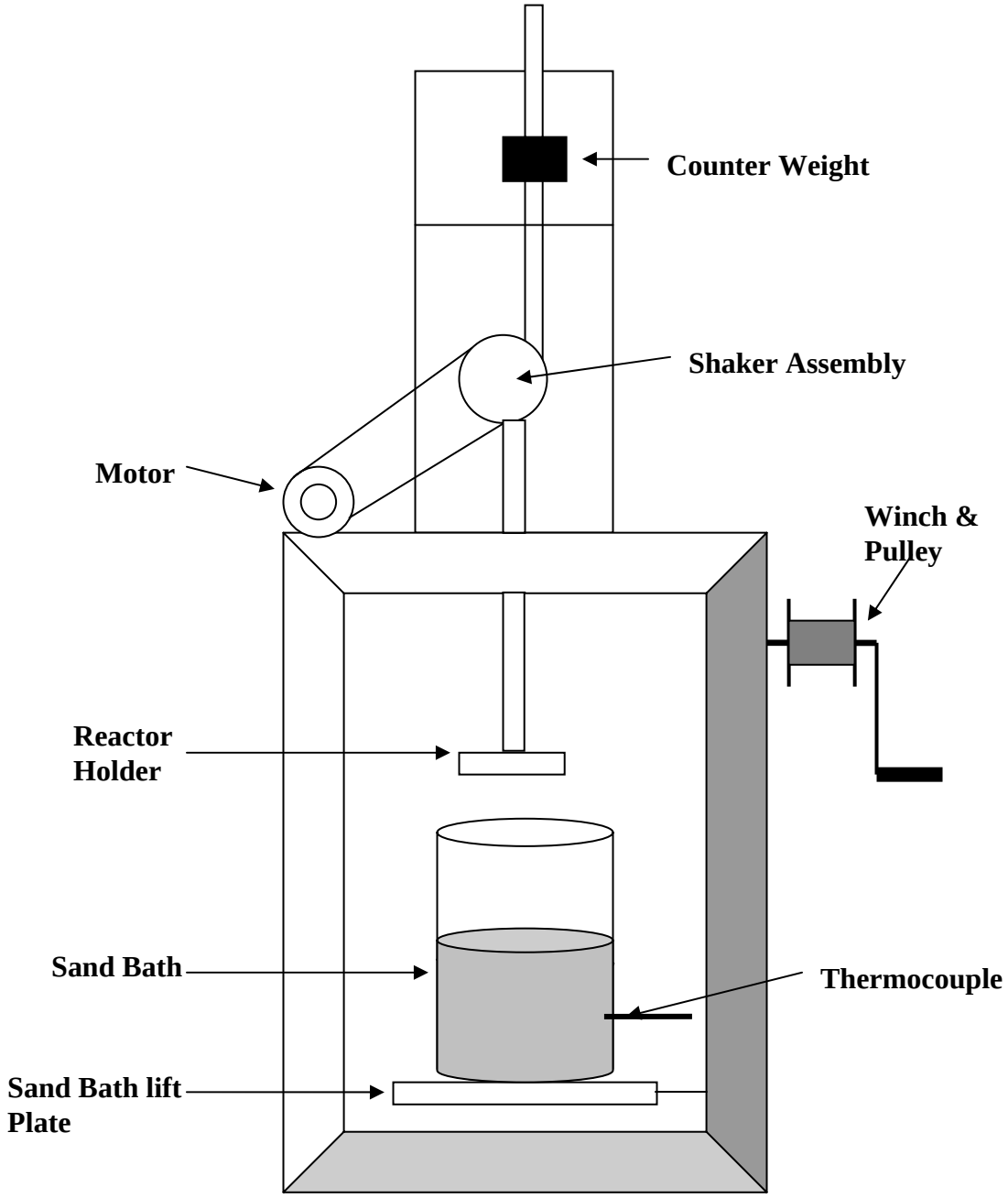


Figure 3.2 Overall reactor system showing sand bath and shaker mechanism

3.2.4 Reactor Charging

Reactants were weighed on an analytical balance to the nearest 0.1 mg and then added to the reactor. The coal-derived solvent was placed in the reactor first. Since the coal liquids are quite viscous, their mass was measured by difference (initial weight of the solvent container was determined and after solvent was added to the reactor, the final weight was determined, the difference between these two weights gave the weight of solvent added to the reactor). Once their mass was determined, the appropriate amount of coal was added to the reactor, based on the desired solvent-to-coal ratio. Finally, three stainless steel ball bearings were weighed and added to the reactor. These help to mix the contents of the reactor during reaction. Once all the reactants were charged, the open end of the reactor was sealed according to the above procedure.

3.2.5 Gas Charging

The hydrogenation reactions were run under either a nitrogen or hydrogen atmosphere. This insured that oxygen would not react with the coal, promoting polymerization and the production of large insoluble coal fragments. Air was removed from the reactors by using a pressure purge cycle. The reactors were pressurized to 1000 psig initially with hydrogen or nitrogen (depending on the specific hydrogenation run) and checked for leaks by immersion into water. The purge valve was then slowly opened to allow the reactor to reach atmospheric pressure. Opening the purge valve slowly was essential so that none of the reactor charge was lost during depressurization. This pressurization and release process was repeated two more times after which the oxygen concentration dropped down to less than 0.0005 %.

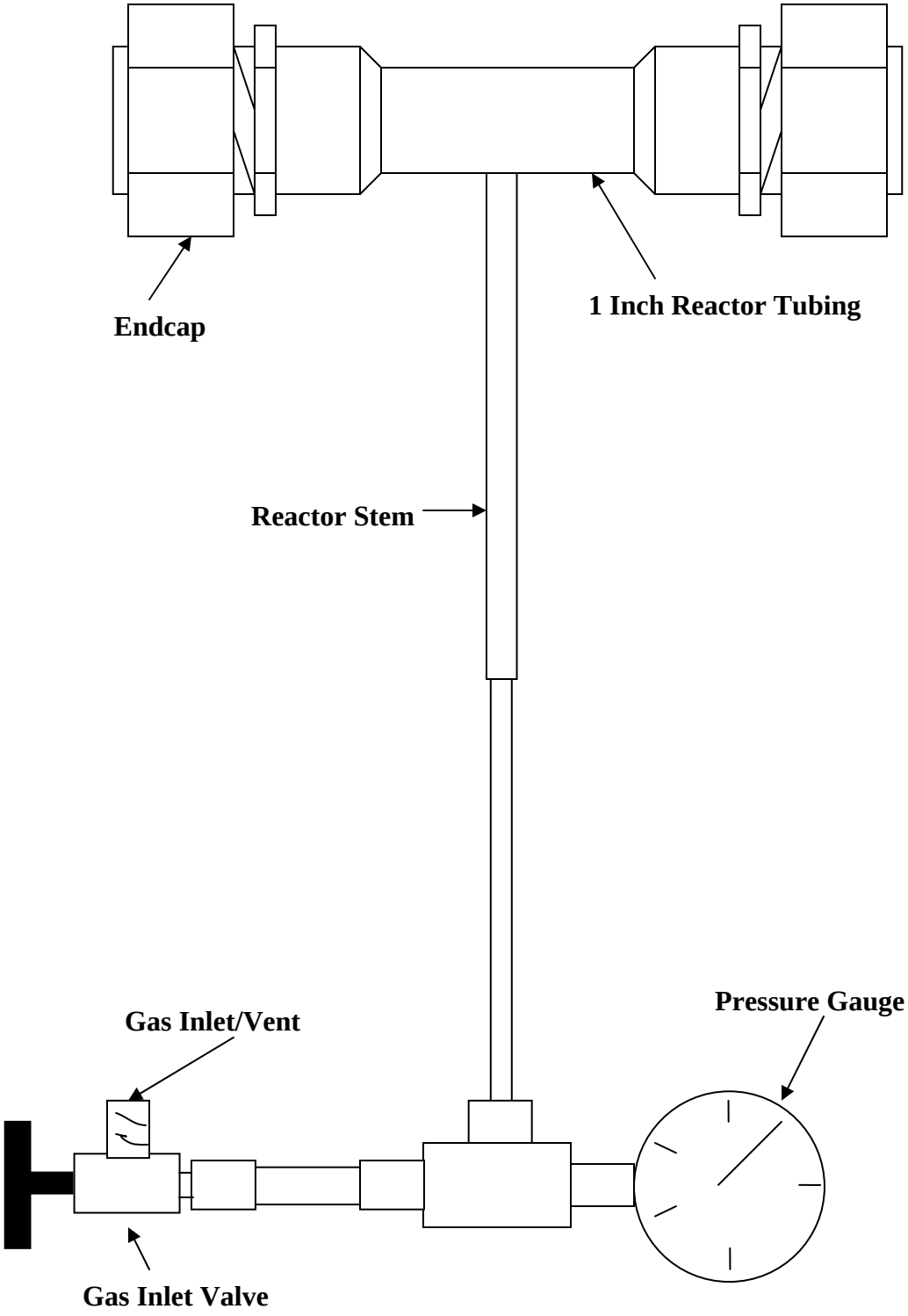


Figure 3.3 Overall View of the 50 mL Tubing Bomb Microreactor

Finally, the reactor was pressurized to the final desired cold reaction pressure. The gas inlet valve of the tubular reactor was then closed and capped with a Swagelok plug.

3.2.6 Reaction Procedure

Once the reactors were charged with reactants and gas, they were placed in the reactor holder above the fluidized sand bath. The reactor holder was attached to a shaking mechanism used during the reaction. After securing the reactors in the holder, the shaking mechanism was turned on, and the speed was adjusted so that the reactors were vertically agitated at approximately 400 rpm with a stroke of approximately 1.5 inches.

The reactors were then rapidly heated by immersion into the sand bath by raising the sand bath using a winch-and-pulley system. The sand bath was raised until the hot sand completely covers the reactor bodies. The temperature of the bath was then adjusted to the desired reaction temperature. Finally, a stopwatch was started to count down from 58 minutes. The extra two minutes (total reaction time was to be 1 hr) allowed time to remove the reactors from the sand bath and quench the reaction.

Once the reaction time had elapsed (58 minutes), the sand bath was lowered by means of the winch-and-pulley system. The agitator was slowed and then turned off. The reactors were removed from the holders and placed in a cold water bath. This served to cool the reactors quickly and quench the hydrogenation reactions.

3.2.7 Product Collection

The products of all the reactions were viscous fluids interlaced with some solid particles. The reactor was placed in a vise and the Swagelok plug was removed from the gas inlet valve. Then one end cap was slowly removed (so that the pressure could be released). The reactor was not vented through the gas inlet valve in order to keep the hydrogenation products in the main body (not the stem or pressure gauge) for ease of cleaning the reactor. A small brush was used to clean any sand away from the reactor threads. The end cap was then replaced and only hand tightened. The reactor was flipped in the vice and the same procedure was used to loosen the other end cap.

A 500-mL flat-bottom boiling flask was placed in a clamp in a fume hood and fitted with a glass funnel. One end cap of the reactor was removed and the reactor was clamped over the funnel allowing its contents to drain into the funnel. A heat gun fanned across the reactor body facilitates this process. Once the products stop dripping, the reactor was filled with THF. A stainless steel spatula was used to scrape the sides of the reactor while it contains THF. The THF was then drained into the boiling flask. This process was repeated several times until all the reaction mass was washed from the reactor. The transfer of the reaction mass from the reactor must be quantitative since the subsequent mass balance and processing steps depend on this procedure.

The end cap was then placed on the open end of the reactor, and the reactor was turned upside down over the funnel. The opposite end cap was now removed and the reactor was again washed with THF several times. Next, both end caps were removed and the final particulates left in the reactor were washed into the flask. The gas inlet valve was opened and THF was used to flush any matter from the reactor stem. The end

caps were then scraped and washed out with THF. Finally, the funnel was washed with THF and removed from the flask.

3.2.8 THF Extraction

The 500-mL flat bottom flask containing the coal/solvent/THF solution was filled (if needed) with fresh THF until it was approximately ¾ full. The flask was placed in a heating mantle and fitted with a simple water-cooled condenser. The cooling water was turned on and the heating mantle temperature was adjusted using a variac. The power was set so that a rolling boil (≅75 °C) was obtained. The contents of the flask were allowed to boil overnight (usually 12-16 hours).

The flask was then cooled to room temperature. The contents of the flask were centrifuged for 30 minutes at 2000 rpm in a glass centrifuge bottle to effect better separation. The liquid portion of the centrifuged product was poured into a Buchner filtering funnel that is under vacuum suction. The filtering funnel was fitted with a pre-weighed piece of filter paper. Following filtration, the solid product (residue) was washed with THF while in the filter funnel. The residue produced by centrifugation was further washed with THF for any retained products and again centrifuged for 15 minutes. Finally, the residues produced by centrifugation and vacuum filtration were combined to form the THF insoluble fraction.

The filtrate was poured into a clean, weighed 250-mL flat bottom flask. The THF in the filtrate was removed by rotary evaporation and collected for later use. The rotary evaporation was done at ambient pressure in a Buchler Instrument Rotary Evaporator, which involved heating the filtrate to around 100 ^{o}C in a preheated oil bath, while

rotating at a set rpm of 90. THF vapors were condensed via a water-cooled condenser and collected into a separate flask as clean THF. The soluble product (extract) was set aside for further processing.

The THF insoluble residue was placed in a vacuum oven (60 °C and 25-30 mm Hg) and allowed to dry overnight (16-20 hours) under a nitrogen purge (100 cc/min). The dried residue was then weighed and the amount of THF insoluble product was determined. This weight was used to calculate the overall conversion using Equation 3-1. The coal-alone conversion was also calculated using Equation 3-2 [13].

$$\%\,\text{Overall Conversion(daf)} = \frac{[(\text{Mass of Dry Coal} + \text{Solvent}) - (\text{Mass of THF Insolubles})]}{\text{Mass of Coal (daf)} + \text{Solvent}} \times 100 \qquad 3\text{-}1$$

$$\%\,\text{Coal Conversion (daf)} = \frac{[(\text{Mass of Dry Coal}) - (\text{Mass of THF Insolubles})]}{\text{Mass of Coal (daf)}} \times 100 \qquad 3\text{-}2$$

It should be noted that for purposes of calculating the coal-alone conversion, all the THF insoluble matter was assumed to come from the coal only and not from the added solvent. Several preliminary reactions were performed using NMP as the extraction solvent, but a large mass loss was observed for the process. The majority of this mass loss occurred during the removal of NMP from the soluble products. Since NMP has a boiling point (202 °C) in the range of many of the light products (particularly those to be collected as the recycle solvent), during the roto-evaporation many of the reaction products were lost. Because the main goal of this research was to isolate a possible recycle solvent, a solvent with a lower boiling point, THF (b.p. 66 ^{o}C), has been employed.

3.2.9 Product Isolation

Once the THF was removed from the extract, the THF-soluble hydrogenation products were separated using vacuum distillation. This was performed using the setup as shown in Figure 3.4. The THF soluble product was gradually heated under vacuum until vapors of liquid products, which were fractions of the coal-derived solvent, start separating out. The flask containing the THF solubles and the part of the condensing tube attached above the flask were covered with glass wool insulation to avoid products condensing in the distillation flask. These separated products were condensed in another flask immersed in a dry ice bath. The dry ice bath helps the quenching process and prevents the lighter products from escaping to the vacuum pump cold trap. The typical distillation conditions were 270-280 ^{o}C temperature and about 30 mm Hg vacuum. The residue from the vacuum distillation was considered to be the soluble coal product (pitch). The distillate was the recovered solvent which would be recycled back to the process. The vacuum distillation was carried out in such a way so as to isolate as much solvent as possible, so that a sufficient quantity was extracted from the process in order to maintain the same coal-to-solvent ratio in the susbsequent hydrotreatment run using coal and the separated recovered solvent. However temperatures above 300 ^{o}C were not exceeded as too much viscous material separated out and got stuck in the condensing tube. This material was very difficult to remove. The recovered solvent was isolated and set aside for further use as the hydrogenation solvent.

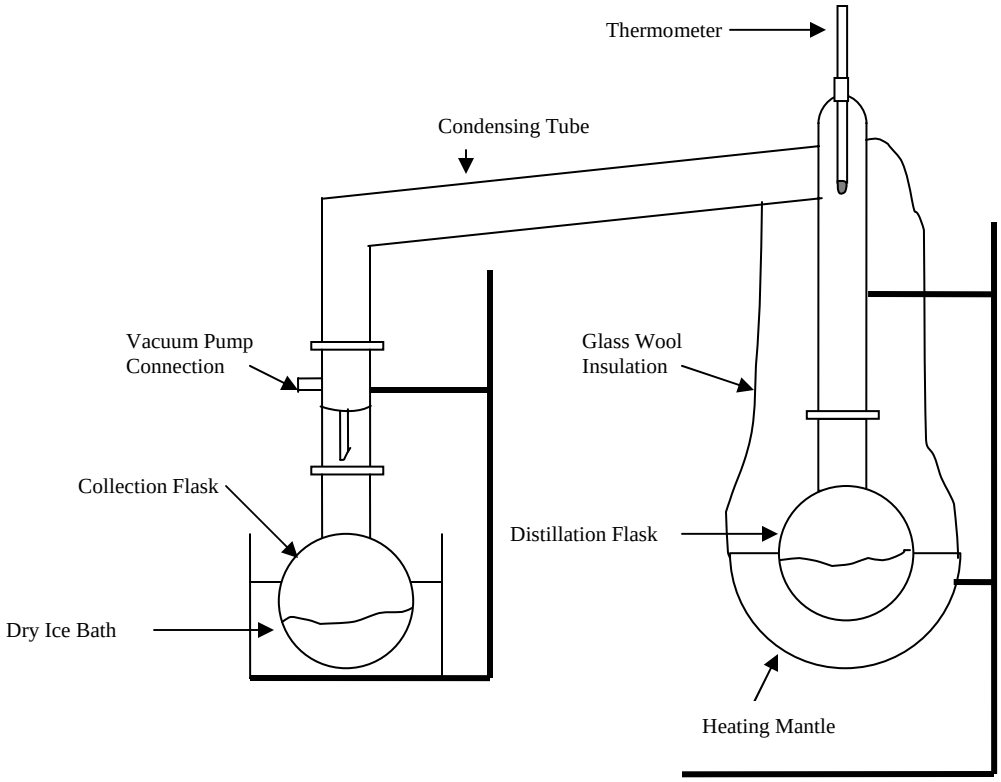


Figure 3.4 Vacuum distillation setup to separate the recovered solvent from the pitch product.

3.3 Characterization Techniques for Cokes and Pitches

The end use of the pitches is determined by their physical and chemical properties. Thus it is important to characterize the pitches based on their properties by some common techniques as mentioned below. This section also explains the standard procedure of doing these tests. The techniques in this research to characterize the pitch product were softening point, ash content, coking value, optical microscopy and proton NMR.

3.3.1 Softening Point

For pitches a distinct melting point cannot be determined because pitch is not a single, pure compound. The softening point is an ASTM test which reflects the ability of a sample to flow a prescribed distance. The measurement gives some insight into the molecular weight distribution of the species present in the pitch. In general, the higher the average molecular weight, the higher is the softening point. It can be beneficial in determining the end use of the pitch. For example a pitch having a low softening point (around 100 ^{o}C) can have applications such as binder or impregnation pitch. On the other hand, a pitch with high softening (around 200-250 ^{o}C) can be used for fiber spinning or coke making.

The softening point was determined by means of a Mettler FP80HT central processor and a Mettler dropping cell. The ASTM D3104 procedure was used in the determination. The sample holder was filled with a sample and was heated until melting occurs. The sample was then cooled and allowed to settle and additional sample was added and melted until the holder was full. This whole procedure was done in a nitrogen atmosphere to avoid smoking of the sample at higher temperatures. The sample holder was then placed in the dropping cell, which was heated at a rate of 2 ^{o}C/min. The softening point temperature was automatically recorded when the sample starts flowing downward through a hole in the bottom of the holder and breaks a beam of light below the sample holder.

3.3.2 Ash Content

The amount of inorganic impurities present in the pitch sample was determined as the ash content. These impurities were derived from the inorganic material present in the original coal sample, which is basically the mineral matter in the coal. These inorganic materials were converted to inorganic oxides during the combustion process of the ash determination. Because this mineral matter is considered as an impurity in the final carbon artifacts, it is important for the ash content of the pitch to be low.

The ash content was determined using a Fisher Isotemp Programmable Furnace Model 497. The test was done according the ASTM standard D3174. Approximately 0.5 to 1 gram of sample was placed in a dry pre-weighed crucible and the crucible was partially covered with a lid. The crucible was heated in air in the furnace at a rate 5 ^{o}C/min upto 500 ^{o}C and then at a rate of 3 ^{o}C/min upto 750 ^{o}C for 180 minutes and then cooled to ambient conditions at a rate of 10 ^{o}C/min. The weight of the sample remaining over the original sample weight gives the ash content.

3.3.3 Optical Microscopy

The optical texture of cokes can be determined by optical microscopy with a polarized-light microscope. The optical texture gives information regarding the surface and graphitization properties of the coke sample. The texture can range from an isotropic carbon (small, uniform domains) to anisotropic carbon (large, elongated domains). The commercial application of the coke sample depends on where it falls in the range of isotropic to anisotropic texture.

The optical structure was determined by means of a polarized-light optical microscope, Zeiss Axiostop, West Germany. The sample was dispersed in an epoxy resin mold, polished, and observed under polarized light. The domain size determines the optical texture. Isotropic coke has very small domains (< 0.5 micron) while an anisotropic coke has large elongated domains (> 100 micron).

3.5.4 Elemental Analysis

Elemental analysis gives the elemental composition of the samples. The measurements can be used to calculate the hydrogen/carbon ratio, which is an important property to compare products from different feedstocks. It can also be used to determine out the hydrogen uptake by the product during the hydrogenation reactions and to compare the fresh and recycle solvents obtained from the process. Finally it gives the level of impurities like nitrogen and sulfur in the product pitch.

Elemental analysis of coal, solvents, pitches, recycle solvents and residue was carried out using a Flash EA-1112 CHNS-O elemental analyzer. It gives the weight percentage of carbon, hydrogen, nitrogen, sulfur. Oxygen was calculated by difference. The sample, weighed in a tin cup, was dropped into a reactor maintained at 900 ^{o}C. The complete combustion of sample occurs in the presence of excess of oxygen and the oxides of C,H,N and S are sent for chromatographic separation and determination. The elemental analyzer was calibrated using a standard compound whose C, H, N and S contents are known accurately. By comparing the C, H, N and S peaks obtained from the standard and the sample, the corresponding values for the samples were determined.

3.3.5 Coking Value

The coke yield determines the amount of carbon residue remaining after hydrogen and volatile matter were removed by thermal treatment, by heating the pitch in the absence of air. The heating process eliminates these volatiles and the pitch is transformed into coke when carbonization is complete. Most commercial applications require a coke yield of 50 to 60 percent by weight.

The ASTM standard D189 was used in determination of coke content, in which the coking value was obtained by measuring the carbon residue after directly heating the sample in a crucible in a high-temperature flame of a burner. The coking value can also be determined by the method developed at WVU. A known sample was placed in a crucible, which was then immersed into coke breeze contained in a larger crucible and heated in a Fisher Scientific Isotemp Programmable Furnace at a rate of 5 ^{o}C/min upto 600 ^{o}C for 2 hours. The sample was then cooled to room temperature at a rate of 10 ^{o}C/min. The mass of residue remaining over the original sample mass gives the coke yield. In this research the WVU method was used to find the coking values of the pitches because this method gives a higher value of coke yield as compared to the Conradson carbon method.

CHAPTER 4

RESULTS AND DISCUSSION

In this chapter, the results of coal conversion in the presence of coal-derived solvents are presented. Firstly, the coal conversions with fresh solvents under standard conditions of hydrotreatment are discussed. Next the same conversions with process-derived recovered solvents are presented and compared with those obtained from fresh solvents. Mass and ash balances of the reactions are presented and the reasons for the losses/gains are evaluated. The dependence of process parameters like temperature and reaction atmosphere are presented as well. Nitrogen was used to run the hydrotreating reactions under an inert atmosphere. Temperature was varied in differentials of 50 ^{o}C from 350 ^{o}C to 450 ^{o}C, to investigate the effect of this parameter on the conversion of the coal to THF solubles. Finally, conversion results from a set of successive hydrotreatment experiments involving only recovered solvents and blends of fresh and recovered solvents are discussed.

Coke yield, ash content, elemental analysis and optical texture of the resultant pitches are assessed. Based on these results optimum continuous hydrotreatment process parameters utilizing the recovered solvents could be established.

4.1 Solvent Evaluation

The first aim of this research is to determine the effectiveness of the three coal-derived liquids HCO, CBB and RCO as hydrogen-donor solvents for coal conversion.

Each of the three coal liquids was used as a hydrogenation solvent under the same standard conditions of 400 ^{o}C, 500 psig cold hydrogen pressure, one hour reaction time and a solvent-to-coal ratio of 5:1. This solvent-to-coal ratio here is higher than what is used typically. The main reason for using a high solvent-to-coal ratio was to obtain an adequate amount of recovered solvent after separation from the pitch, so as to study these recovered solvents separately as recycle solvents in subsequent hydrogenation runs. These coal-derived liquids are characterized according to their ability to convert coal to THF soluble material. Two different methods of measuring their effectiveness were used: (1) the overall conversion based on the total feed (i.e. coal plus solvent) as given by Equation 3.1 and (2) the coal-alone conversion based only on the weight of coal as given by Equation 3.2.

The overall and coal-alone conversion for these liquids at 400 ^{o}C and 500 psig H_2 pressure is shown in Figure 4.1. These results show that the most effective solvent for solubilising coal to THF solubles is CBB with a coal-alone conversion of 43.4 ± 0.9 % while the least effective solvent is RCO with coal-alone conversion of 31.1 ± 0.5 %. Conversion for the solvent CBB is close to HCO showing a conversion of 42.6 ± 0.7 %. The overall conversion of CBB, HCO and RCO are 90.2, 90.1 and 88.2 % respectively. The conversion results are quite different when the coal-alone basis is used. The absolute value of the conversion changed drastically for each solvent from an overall to a coal-alone basis. The reason for the large difference between the values of the two methods of calculating the conversions is that the overall conversion includes solvent in its calculation, while the coal-alone conversion does not. Because the coal liquids exhibit complete solubility in THF to begin with and the use of a high 5:1 solvent-to-coal ratio

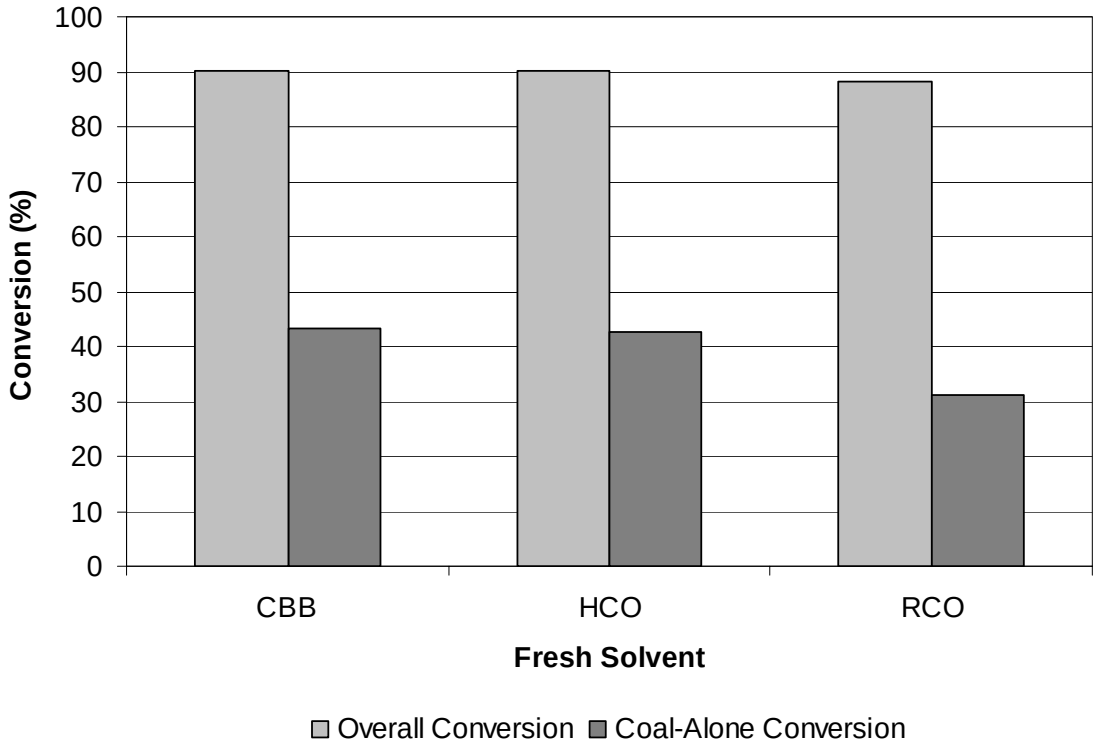


Figure 4.1 Overall and Coal-alone conversion yields with fresh HCO, CBB and RCO at 400 ^{o}C, 500 psig cold hydrogen and one hour reaction time

by weight, the majority of the THF soluble fraction of the hydrogenation products was derived from the solvent itself. Therefore, the effect of changing solvents on coal conversion was swamped by the large amount of solvent that was included in the overall conversion calculation. So, the coal-alone conversion gives a more definitive comparison between the solvents as it does not include any solvent in the THF solubles.

It should be noted that all the THF insolubles come from the coal and not from the solvent. This was in fact tested initially by dissolving the fresh coal-derived solvents in THF and then filtering the solution to check for any solids. The solution looked homogenous and no residue was found on the filter paper. Since the fresh solvents did not contain any THF insolubles, it was safely assumed that these solvents would not form any such material after hydrotreating. This is an important point since the coal-alone conversion is calculated solely from the weight of the residue which is assumed to originate exclusively from the coal.

4.2 Recovered Solvent Evaluation

The second and main aim of this research is to evaluate the effectiveness of the recycled solvent which had been recovered by distillation from the previous hydrotreatment run. Figure 4.2 shows the overall and coal-alone conversion results for the corresponding recovered solvents. The overall conversion results show 90.4, 90.2, 88.3 % conversion for recovered CBB, HCO and RCO respectively. As compared to fresh solvents, the overall conversion is almost the same, because of the solvent continues to dominate the amount of coal and hence very little difference in coal conversion is seen. However the coal-alone conversion gives a better picture.

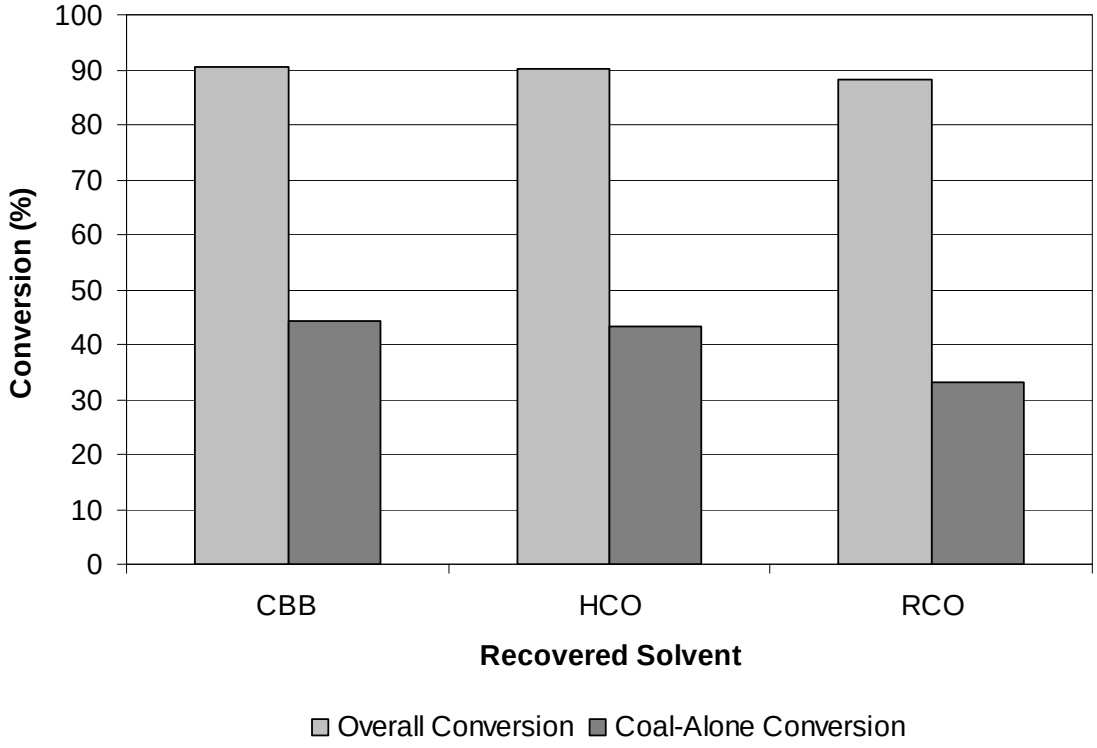


Figure 4.2 Overall and Coal-alone conversion yields with recovered HCO, CBB and RCO at 400 ^{o}C, 500 psig cold hydrogen and one hour reaction time

The results indicate that the coal-alone conversion is 44.2 ± 0.8 %, 43.4 ± 1.1 % and 33.2 ± 1.3 % for recycled CBB, HCO and RCO respectively. The coal-alone conversion shows some difference between the fresh and recovered solvents and suggests that the recovered solvents actually behave comparably or better than the fresh solvent. This behavior can be attributed to the fact that the solvent either gets partially hydrogenated in the process of hydrogenating the coal or the distillation concentrates more H-donors in the recovered solvent. Hence the recovered solvent is able to perform better in subsequent hydrogenations. In addition, the mineral matter in the coal may be catalytically active in hydrogenation reactions and could support hydrogenation of the solvent along with coal. In fact this is supported by elemental analysis which shows a higher hydrogen-to-carbon ratio in the recovered solvent compared to fresh solvent. This will be discussed in detail in a later section.

4.3 Mass Balances with Fresh Solvents

A mass balance was performed on each hydrogenation run including the three solvents being tested under the reaction conditions as shown in Table 3.3. The results of the mass balance for all the trials with different solvents are shown in Table 4.1. Mass input includes total coal and solvent while mass output includes the separated products: THF insoluble residue, pitch and the recovered solvent.

The results of the mass balances with the fresh solvents showed a negative mass balance which means that some mass was lost in each of these hydrogenation runs. The average mass loss was 7-10 % for the fresh solvents. The following reasons could account for the mass loss. Firstly, during the THF separation by rotovaporization, some

very light boiling volatiles could be lost with the recovered THF. This was suggested by the faint coloration of the recovered THF. Usually this mass loss would be negligible, since THF is a low-boiling solvent and it is very unlikely that the coal-derived products would have much light species in the boiling range of THF. The majority of the mass loss occurred during the vacuum distillation step which separated the pitch and the recovered solvent. Since vacuum was used in this separation, some of lighter boiling compounds would not be condensed at that low pressure. These non-condensibles would pass the distillate flask and get trapped in the cold trap of the vacuum pump. This was confirmed by periodically checking the cold trap flask and noting some quantity of liquid. Lastly, some of the lights may have been trapped in the centrifuge glass bottle with THF insolubles, and would eventually get lost in the vacuum oven cold trap during drying of the THF insolubles. This mass loss could be minimized by washing the residue repeatedly with THF till a clear THF decanting solution appears after centrifugation. The finding though was that even after repeated washings it was very difficult to get a clear THF decantant liquid, so it is believed that some of the mass loss could take place in this way.

Some appropriate measures were taken to minimize the mass loss. Firstly, in the vacuum distillation process, the distillate collection flask was immersed in dry ice in an attempt to condense the lighter species that were escaping to the cold trap. In this way the loss during the vacuum distillation step could be minimized, though not eliminated. It was observed in every distillation run that the condenser had a coating of the distillate material, which would not flow even after heating with a heat gun. When this material left over in the condenser was not accounted for, the mass loss was greatly increased.

Table 4.1 Overall mass balances of the coal hydrogenation reactions with fresh solvents

Run[a]	Trial	Coal (g)	Fresh Solvent (g)	Total Input (g)	Pitch (g)	THF Ins. (g)	Rec. Solv. (g)	Total Output (g)	Input - Output (g)	Loss (%)
1	A	4.001	20.02	24.021	2.49	2.3119	17.65	22.452	1.569	6.5
1	B	4.0032	20.1	24.1032	3.01	2.4008	16.87	22.2808	1.8224	7.6
1	C	4.0021	20.2	24.2021	2.88	2.3566	17.1	22.3366	1.8655	7.7
1	D	4.0019	20.1	24.1019	2.72	2.3801	16.55	21.6501	2.4518	10.1
2	A	4.002	20.2	24.202	2.71	2.4201	17.22	22.3501	1.8519	7.6
2	B	4.0056	20.3	24.3056	2.967	2.371	17.29	22.628	1.6776	6.9
2	C	4.0021	19.92	23.9221	3.8	2.3654	16.2	22.3654	1.5567	6.5
2	D	4.0031	20.2	24.2031	3.05	2.4198	16.41	21.8798	2.3233	9.6
3	A	4.0001	20.3	24.3001	3.94	2.8429	15.87	22.6529	1.6472	6.7
3	B	4.0032	20.1	24.1032	3.98	2.8156	15.1	21.8956	2.2076	9.1
3	C	4.0012	20.4	24.4012	4.28	2.8112	14.98	22.0712	2.33	9.7
3	D	3.9988	20.02	24.0188	3.99	2.8256	15.66	22.4756	1.5432	6.4

[a] Here run 1 is using CBB, run 2 is using HCO and run 3 is using RCO

So, in an attempt to account for this material, its mass was found by difference by weighing the condenser before and after the vacuum distillation and incorporating this weight in the mass balances, thus reducing the errors. Considering so many operations, handling and liquid transfers, an average mass loss of 8 % seems to be quite good for the hydrogenation runs involving fresh solvents.

4.4 Mass Balances with Recovered Solvents

The mass balances with recovered solvents for subsequent runs are shown in Table 4.2. The only difference between fresh and recovered solvent mass balances is that recovered solvents showed a mass loss of 10-13 %. Many of the reasons for mass loss that apply to fresh also apply to the recovered solvents. It is very likely that the recovered solvent is lighter compared to the fresh solvents, as it is a distillate product from the distillation of the mixture of pitch and fresh solvent. This is also suggested by the coloration of the recovered solvents which is less dark than the fresh solvent and also by the hydrogen-to-carbon ratio of the recovered solvent which is greater than the fresh solvent. So, all the factors of mass loss would be even more enhanced for these recovered solvents giving a higher value to the loss.

The errors in mass balance would be transferred to the other calculations which are based on the mass of the reactants and the recovered products. These calculations would include ash balances, carbon balances and hydrogen balances.

Table 4.2 Overall mass balances of the coal hydrogenation reactions with recovered solvents.

Run[a]	Trial	Coal (g)	Rec. Solvent (g)	Total Input (g)	Pitch (g)	THF Ins. (g)	Rec. Solv. (g)	Total Output (g)	Input - Output (g)	Loss (%)
4	A	4.001	20.1	24.101	2.988	2.3014	16.125	21.4094	2.6916	11.2
4	B	4.0021	20.4	24.4021	3.1088	2.3708	15.58	21.0596	3.3425	13.7
4	C	4.008	20.5	24.508	3.2756	2.3244	15.28	20.88	3.628	14.8
4	D	4.0039	19.92	23.9239	2.878	2.3446	16.4	21.6226	2.3013	9.6
5	A	4.0012	20.2	24.2012	3.2931	2.3431	15.49	21.1262	3.075	12.7
5	B	4.0036	20.1	24.1036	2.656	2.405	16.36	21.421	2.6826	11.2
5	C	4.001	20.2	24.201	2.786	2.3203	16.19	21.2963	2.9047	12
5	D	4.0016	20	24.0016	2.9821	2.3848	16.02	21.3869	2.6147	10.9
6	A	4.0026	20.4	24.4026	2.6822	2.6991	15.98	21.3613	3.0413	12.4
6	B	4.0001	19.9	23.9001	3.2612	2.7691	15.14	21.1703	2.7298	11.4
6	C	4.0039	20.1	24.1039	2.9932	2.7982	16.12	21.9114	2.1925	9.1
6	D	4.0013	20.3	24.3013	2.7899	2.7208	15.66	21.1707	3.1306	12.9

[a] Here run 4 is using Rec. CBB, run 5 is using Rec. HCO and run 6 is using Rec. RCO

4.5 Ash Balance

The ash content is critical in the hydrogenation reactions and it is desired for the pitch product to have as low an ash value as possible. It is not possible to eliminate ash entirely from the pitch but there are steps to minimize it, described later. The recovered solvents were tested for ash and found to be negligible. Hence they were disregarded in the ash balance calculation whereas all the ash is concentrated in the THF insolubles. Similarly, this applies to reactants as well, where all the ash is in the coal and negligible ash is in the coal-derived solvents. Most of the ash from the coal is concentrated in the THF insoluble fraction as the mineral matter is not extracted into the coal-derived solvent. The THF insoluble fraction basically contains the mineral matter and the unconverted organic matter from the coal. All this mineral matter is converted into ash after oxidation. The ash content is found as a weight percent by the ash test described in Section 3.3.2. Then the actual mass of ash in the species is determined by multiplying the ash percentage by the corresponding mass of that species from the mass balance. The ash test had a small relative error of around ± 2 %.

The results of the ash balance for fresh and recovered solvent are shown in Tables 4.3 and 4.4 respectively. The results show a random distribution of gain and loss of ash in the species. Since the ash balance is calculated from the mass balance, any errors in the mass balance would propagate in the ash balance as well. The ash content in the coal and the THF insolubles dominates the ash balance calculation as can be seen from the results. The positive ash balance values correspond to the negative mass balance values. This is because, as mass is lost, which is typically the lighter hydrocarbons, the ash in the remaining heavier products would be concentrated thus giving a higher ash value as

compared to the actual ash in the original samples. Hence positive values of ash balance are more the norm. Most of the values show a positive balance and are consistent with the negative mass balances. But some do show negative values of ash balance. This can be attributed to the fact that sometimes the separation of THF solubles from the insolubles was not entirely complete. It has already been mentioned earlier, that even multiple centrifugations would not give clear THF decanting liquid, suggesting some solubles trapped in the THF insolubles. This phenomenon would decrease the ash in the dominant THF insolubles fraction, thus giving negative ash balance values. As seen in Table 4.4, the ash in the recovered solvent is negligible since the starting fresh solvent had a very small amount of ash. So the ash in the recovered solvent is not shown in Table 4.4 and the only ash entering the process is from the starting coal.

4.6 Hydrogenation Reactions Pressure Profiles.

All the hydrogenation reactions were started with initial 500 psig cold gas pressure. Pressure was monitored with time during the course of the reaction and following quenching. The pressure profiles are important and give valuable information such as the maximum pressure under high temperature conditions, the average rate of rise or fall of pressure during the reaction and the cold pressure at the end of the run. This information gives significant insight into the chemistry of the reaction. For example the maximum rise in pressure at hot conditions reflects the molecular weight distribution of the solvent. The rate of pressure fall under a hydrogen atmosphere gives an indication of how fast hydrogen is being consumed in the reaction. The rate of pressure rise under a nitrogen atmosphere gives an indication of how fast the volatiles are coming off the

Table 4.3 Overall ash balances of the coal hydrogenation reactions with fresh solvents

Run[a]	Trial	Coal Ash (g)	Solvent Ash (g)	Ash Input (g)	Pitch Ash (g)	THF Ins. Ash (g)	Ash Output (g)	Input - Output (g)	Loss (%)
1	A	0.2240	0.0120	0.2360	0.0039	0.2138	0.2177	0.0183	7.7
1	B	0.2241	0.0120	0.2361	0.0048	0.2220	0.2268	0.0092	3.9
1	C	0.2241	0.0121	0.2362	0.0046	0.2179	0.2225	0.0136	5.7
1	D	0.2241	0.0120	0.2361	0.0043	0.2201	0.2244	0.0116	4.9
2	A	0.2241	0.0161	0.2402	0.0067	0.2371	0.2438	-0.0036	-1.5
2	B	0.2243	0.0162	0.2405	0.0074	0.2323	0.2397	0.0007	1.7
2	C	0.2241	0.0159	0.2400	0.0095	0.2318	0.2413	-0.0013	-0.5
2	D	0.2241	0.0161	0.2402	0.0076	0.2371	0.2447	-0.0045	-1.9
3	A	0.2240	0.0182	0.24227	0.0110	0.2331	0.2441	-0.0019	-0.8
3	B	0.2241	0.0181	0.2422	0.0111	0.2308	0.2419	0.0003	0.2
3	C	0.2240	0.0183	0.2423	0.0119	0.2305	0.2424	-0.0001	-0.04
3	D	0.2239	0.0180	0.2419	0.0111	0.2316	0.2427	-0.0008	-0.3

[a] Here run 1 is using CBB, run 2 is using HCO and run 3 is using RCO

Table 4.4 Overall ash balances of the coal hydrogenation reactions with recovered solvents.

Run[a]	Trial	Coal Ash (g)	Pitch Ash (g)	THF Ins. Ash (g)	Ash Output (g)	Input - Output (g)	Loss (%)
4	A	0.2240	0.0047	0.1956	0.2003	0.0236	10.5
4	B	0.2241	0.0049	0.2015	0.2064	0.0176	7.8
4	C	0.2244	0.0052	0.1975	0.2027	0.0216	9.6
4	D	0.2242	0.0046	0.1992	0.2038	0.0203	9.0
5	A	0.2240	0.0082	0.1921	0.2003	0.0236	10.5
5	B	0.2242	0.0066	0.1972	0.2038	0.0204	9.1
5	C	0.2240	0.0069	0.1902	0.1971	0.0269	12
5	D	0.2240	0.0074	0.1955	0.2029	0.0210	9.4
6	A	0.2241	0.0075	0.2132	0.2207	0.0033	14.7
6	B	0.2240	0.0091	0.2187	0.2278	-0.0038	-1.7
6	C	0.2242	0.0083	0.2210	0.2293	-0.0051	-2.2
6	D	0.2240	0.0078	0.2149	0.2227	0.0012	0.6

[a] Here run 4 is using Rec. CBB, run 5 is using Rec. HCO and run 6 is using Rec.RCO

reacting mixture. The final cold pressure also confirms gas consumption of the reactive gas atmosphere. For example hydrogen consumption in the overall reaction gives a final cold pressure less than the initial cold pressure whereas a reverse trend is observed for the nitrogen atmosphere. The difference of final and initial cold pressure indicates either the extent of hydrogen uptake by soluble species and/or solvent in the hydrogen atmosphere or the amount of non-condensibles released from the coal/solvent during the reaction in the nitrogen atmosphere. From this difference in pressures the moles of hydrogen consumed or the moles of non-condensibles released could be estimated.

Figure 4.3 shows the pressure profiles for the fresh solvents namely HCO, CBB and RCO under the hydrogen atmosphere. It can be observed that since the atmosphere is hydrogen, the final cold pressure is less than the initial cold starting pressure. RCO gave the maximum pressure rise under hot conditions, indicating it has a lower molecular weight distribution than the other solvents. The difference between the final and initial cold pressure is maximum for CBB, suggesting that more hydrogen is consumed by it to solubilise the coal and hence more soluble species are produced compared to the other solvents. This is in fact found to be true. For the hydrogenation runs, assuming all the pressure difference is due to consumption of hydrogen, the estimated weight percent of hydrogen consumed was found to be 0.06 % on the total feed basis.

Figure 4.4 shows the pressure profiles for recovered solvents obtained from runs using the three fresh solvents. For the most part, the profiles are the same, the only difference being the final pressure is somewhat lower than the corresponding pressure for the fresh solvents. Also it can be observed that the maximum pressure and the rate

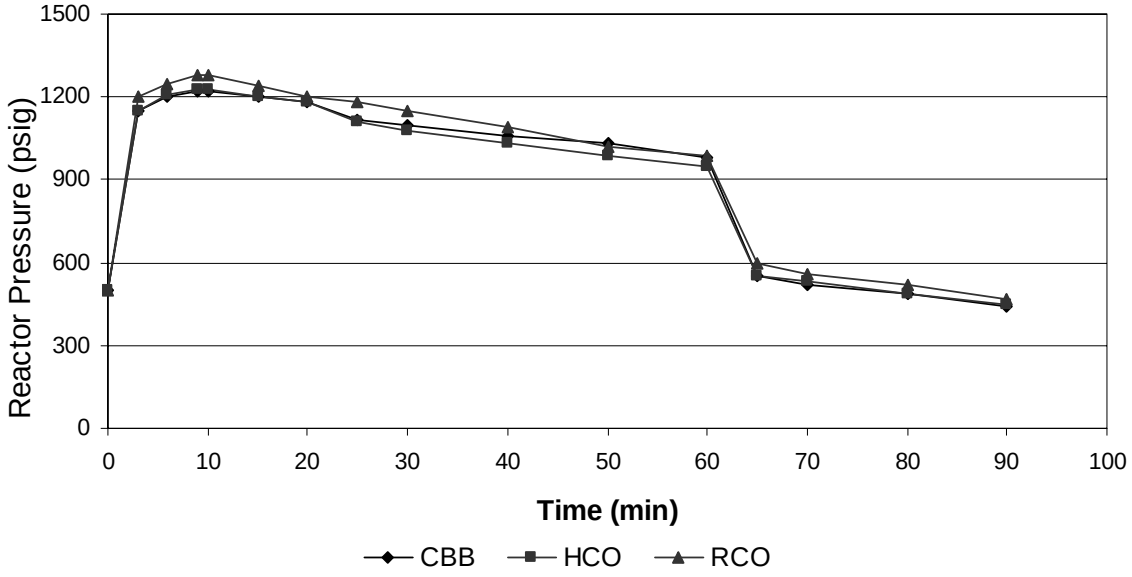


Figure 4.3 Pressure profiles for fresh solvents CBB, HCO and RCO at 400 ^{o}C, 500 psig cold hydrogen and one hour reaction time

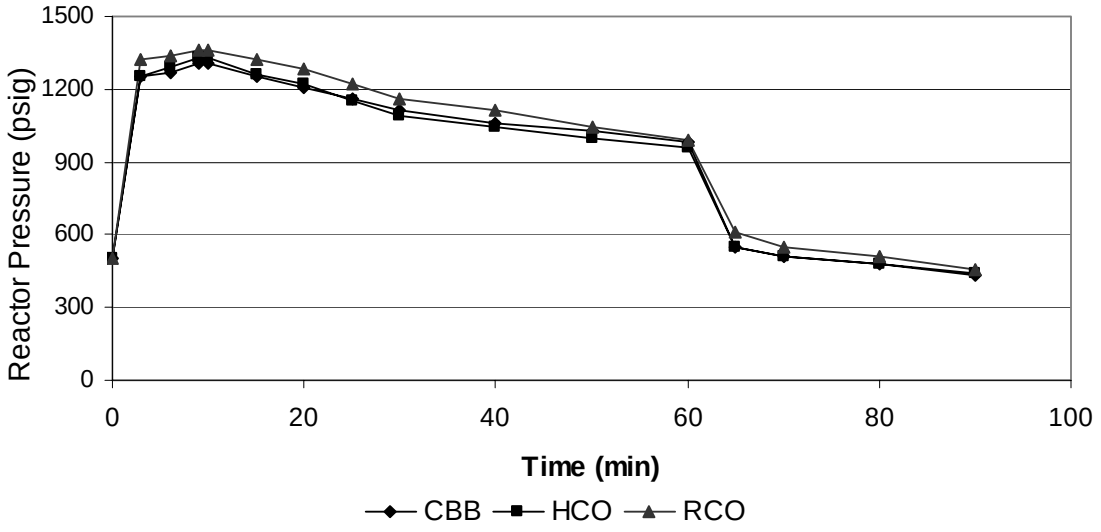


Figure 4.4 Pressure profiles for recovered solvents CBB, HCO and RCO at 400 ^{o}C, 500 psig cold hydrogen and one hour reaction time

of pressure decrease are higher for these recovered solvents. It suggests that the recovered solvents should be lighter and may give higher conversion than the fresh solvents. This is borne out by the data for the most part.

4.7.1 Hydrogenation Products

Upon completion of the vacuum distillation, the products of the reaction were separated to form three fractions namely pitch (THF solubles), THF insolubles and the recovered solvent. The latter two products were considered to be by-products of the process and so are not characterized in as much detail as the pitch product. Elemental analysis and ash content were done on these products so that an elemental balance and ash balance could be made. On the primary pitch product, analytical techniques like softening point, ash content, coke yield, and optical texture were performed to compare pitches obtained from this process to the commercial pitches available on the market. The vacuum distillation conditions were maintained the same for the separations involving different solvents and were 30 mm Hg vacuum and 270-280 ^{o}C maximum vapor temperature. It should be noted that the final temperature of the distillation residue left in the pot could be well over 280 ^{o}C.

The product distributions for these hydrogenation runs for the three fresh and recovered solvents are shown in Figure 4.5. The product distribution for HCO and CBB appear to be similar while RCO shows some difference. It can be observed that the dominant fraction among the three products is the recovered solvent which accounts for

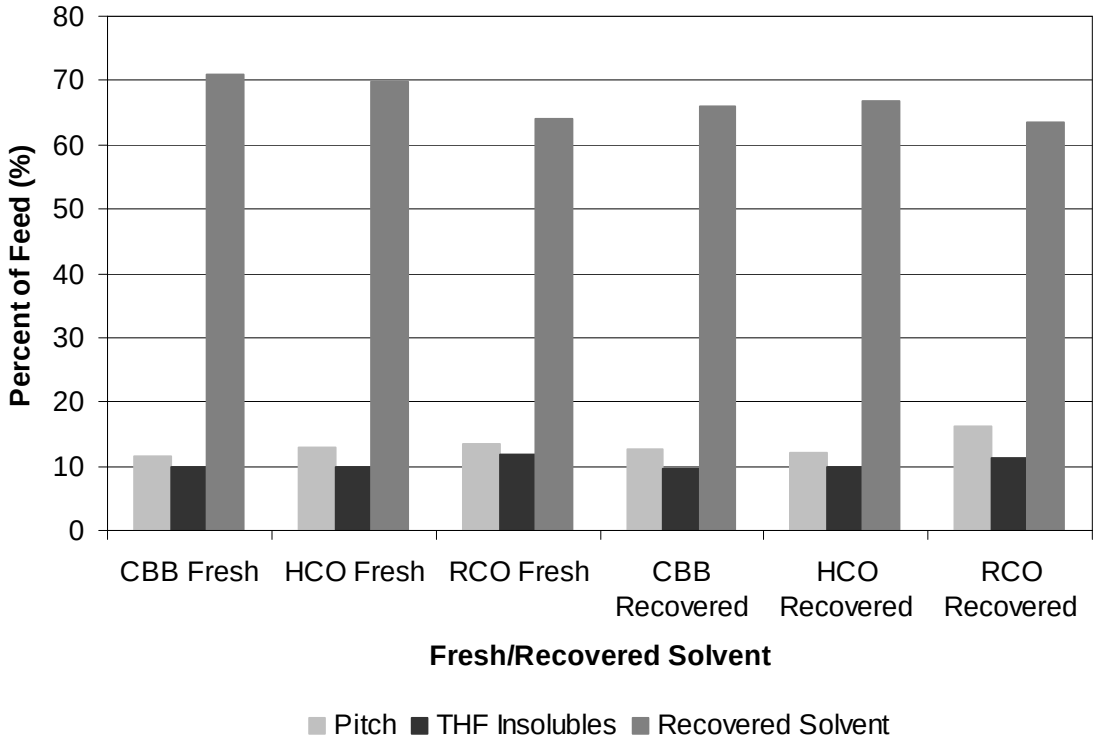


Figure 4.5 Hydrogenation product distribution for fresh and recovered solvents CBB, HCO and RCO at 400 ^{o}C, 500 psig cold hydrogen and one hour reaction time

60-70 % of the original feed amount. The other two fractions, namely the pitch and the THF insolubles, depend upon the coal-alone conversion yields of the corresponding solvents. Since CBB and HCO show similar conversion, these two fractions are close for these two solvents. A general trend is that the quantity of products for runs using recovered solvent is slightly less than that for the fresh solvent. The quantity of recovered solvent is critical here, since the larger the amount, the more that is available for recycle. Also since the recovered solvent is the lightest fraction compared to the other two products, a lower amount of recovered solvent suggests a higher mass loss. For instance RCO shows a low percentage of recovered solvent and hence has a higher average mass loss compared to the other two solvents.

From the above discussion it is clear that a balance must be struck between the amount of solvent distilled and the mass of pitch product. If more pitch product is desired then the amount of recovered solvent decreases, necessitating a larger amount of fresh make-up for subsequent reactions. With very low pitch product, the process might not be economical given that pitch is the primary product. But the fact remains that the balance between these two products is governed by the final properties of the pitch and can be the sole criterion for separation. As discussed in a later section, the pitch properties change depending on the amount of recovered solvent, so in order to obtain a tailor-made pitch, the proper quantity of solvent must be separated.

4.7.2 Ash Content

The ash content of the pitch is a very important property, since ash is considered an impurity in the pitch and hence detrimental to the product quality. Thus it is desired to

have the ash value in the pitch as low as possible. Also the ash content in the final coked product is always more than in the starting pitch. This is because, as the pitch is heated during coking, the volatiles are driven off and the ash gets concentrated in the coke. So, it is very important to control ash in the initial pitch making process. There are two different ways to do this other than by altering the processing steps (the processing steps here are the same for all the runs): 1. Reduce the amount of recovered solvent distilled, so as to increase the lighter components in the pitch or 2. Select a solvent which gives a higher conversion yield from the starting coal. The higher conversion would imply that ash gets concentrated in the THF insoluble fraction as a higher fraction of organics is extracted from the coal.

The ash content is determined by the ASTM method outlined in Section 3.3.2. The relative error in determining ash content of the THF insolubles was small, ± 2 %. In contrast, the relative error of the ash content in the pitch product was found to be ± 4 %. The reason for the high error is the relatively small amount of ash in the pitch as compared to that in the insolubles. Also ash was not found in the recovered solvents as they are the distillate products. So, the two main components of ash content were the pitch and the THF insolubles. Tables 4.5 and 4.6 show the percent ash in these two product fractions for fresh and recovered solvents.

It can be observed that the pitch fraction has a very low ash content of around 0.2-0.3 %, whereas most of the ash is seen in the insolubles. The ash content of the insolubles is around 10 % for the all solvents used. As mentioned previously, the solvent which gave high conversion has a higher ash percentage in the THF insolubles. However the pitch product does not follow the trend of low ash with increased conversion as expected.

Table 4.5 Ash content, coke yield and softening point of the hydrogenation products using fresh solvent.

Fresh Solvent	Ash Content in THF Insolubles (%)	Ash Content in Pitch (%)	Coke Yield (%)	Softening Point (^{o}C)
CBB	9.2	0.16	81.4	129
HCO	9.1	0.25	79.1	122
RCO	8.2	0.28	84.1	158

Table 4.6 Ash content, coke yield and softening point of the hydrogenation products using recovered solvent.

Recovered Solvent	Ash Content in THF Insolubles (%)	Ash Content in Pitch (%)	Coke Yield (%)	Softening Point (^{o}C)
CBB	8.5	0.15	83.1	132
HCO	8.2	0.24	80.6	125
RCO	7.9	0.27	84.9	156

The ash content in the pitch is more random and depends on the variability of the processing steps. The ash in the pitches from runs using the recovered solvents is slightly lower than the corresponding runs using fresh solvent. The same applies to the ash in the THF insolubles.

4.7.3 Coke Yield and Softening Point

The softening point of the pitch gives an indication of the temperature at which the pitch melts and is flowable. The coke yield gives the content of non-volatiles in the sample. Both these techniques are described in Sections 3.3.1 and 3.3.5. The relative error for the coke test was typically ± 1.8 % while that for the softening point was ± 1.5 ^{o}C.

Tables 4.5 and 4.6 show the softening point and the coke yield of the pitch samples for fresh and recovered solvents respectively. These values are at a fixed distillation condition of 30 mm hg vacuum and 270-280 ^{o}C final vapor temperature. It is important to specify the distillation conditions since the pitch properties are highly dependent on them, as will be discussed below. It can be observed from the results that the coke yields of the pitches are in the range of 80-85 % and the softening point is in the range of 130-160 ^{o}C. These values are typically higher than those for commercial binder pitches. As will be discussed later, the optical micrographs of the raw pitches show some development of mesophase. This is due to the rather high temperature the pitch sees in the distillation pot – sometimes higher than 300 ^{o}C. Thus the high coke yield is a consequence of the presence of the mesophase in the pitch. The softening point is rather low for pitches with such high coke yield. This is a result of the continuous isotropic

phase which is controlling the softening point. It is desired to have a high coke yield, to optimize the yield of the final carbon product, whereas the softening point depends on the end application. So, pitches obtained from this process might be useful for applications such as fiber spinning or coke making which require high softening point and coke yield.

As mentioned above, changing distillation conditions imparts different properties to the pitch. Figure 4.6 shows coke yield and softening point changing for the pitch samples obtained when varying amounts of solvent are distilled. The softening point and coke yield values of these pitch samples are plotted against each other in Figure 4.7. It can be observed that a linear trend is followed between these two properties, based on distillation conditions. This can be important commercially, where a variety of tailor-made pitches are required based on the end applications.

4.7.4 Elemental Analysis

The elemental analysis, as outlined in Section 3.3.4, was performed on select hydrogenation runs and done on all the products from the reactions. Only those runs were selected for elemental analysis in which the vacuum distillation conditions were maintained the same. Thus the results could be compared more meaningfully between different solvents. The relative errors in the elemental values for hydrogen and carbon were ± 1.8 % and ± 2.2 % respectively. The errors for nitrogen and sulfur were higher, around ± 8 %, due to the low quantities of these elements. The elemental composition and hydrogen-to-carbon ratios of the selected hydrogenation products are shown in Table 4.7. Here pass 1 refers to reaction with fresh solvent whereas pass 2 represents the reaction run with the solvent recovered from pass 1.

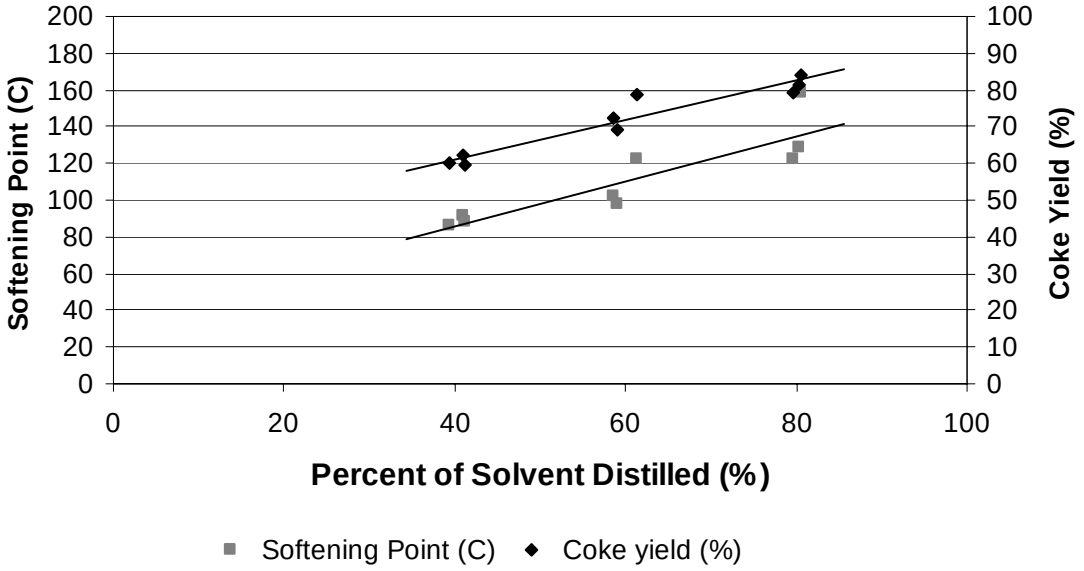


Figure 4.6 Relation between coke yield and softening point for solvents CBB, HCO and RCO at 400 ^{o}C, 500 psig cold hydrogen and one hour reaction time.

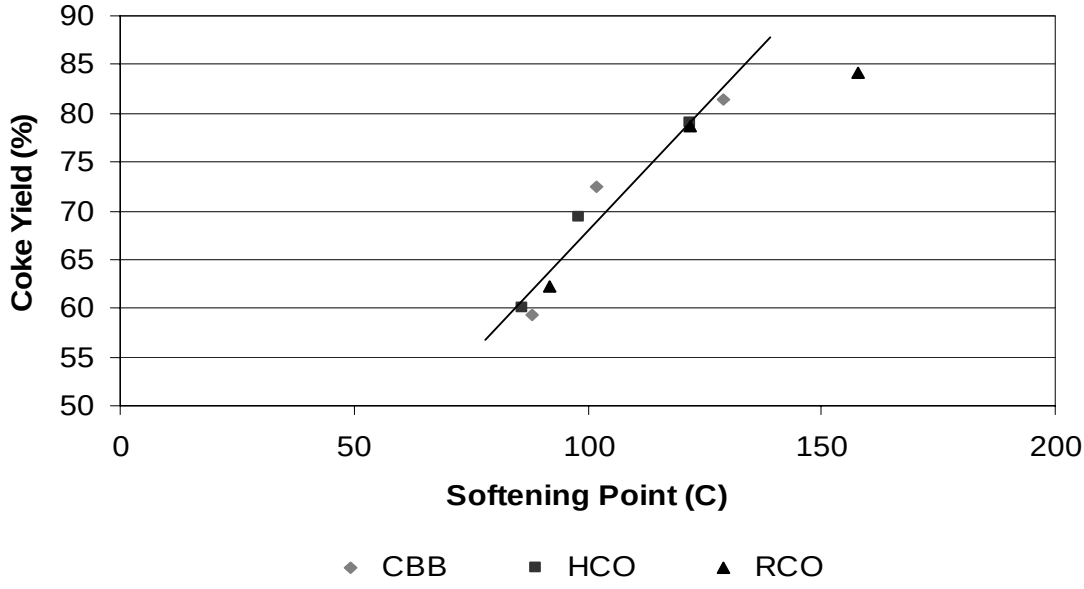


Figure 4.7 Relation between coke yield and softening point for solvents CBB, HCO and RCO at 400 ^{o}C, 500 psig cold hydrogen and one hour reaction time.

It can be observed from Table 4.7 that the hydrogen-to-carbon ratio increases for pass 1 run from THF insolubles to pitch to recovered solvent. This is expected as the solvent is the lightest fraction among the products obtained. It can be noticed that all pitch products have a higher hydrogen-to-carbon ratio than the starting coal, which means hydrogen has been added to the coal organic matrix by hydrotreatment. Also it can be observed that the pass 2 recovered solvent has a higher hydrogen-to-carbon ratio than pass 1 recovered solvent which in turn has a higher hydrogen-to-carbon ratio than the corresponding fresh solvent. This indicates that some hydrogen rich light material is being produced during the hydrogenation runs. This also explains the fact that higher or comparable conversion is obtained when the recovered solvent from the earlier hydrogenation run is used in a subsequent run. But this is not always true for continued recycling, as will be explained in a later section.

The elemental analysis was also used to perform a carbon and hydrogen balance for the reacting and product species. The results of the balances are shown in Table 4.8 and 4.9 for carbon and hydrogen respectively. The carbon balance shows a negative balance suggesting a loss during the process. This is consistent with the fact that the mass balance also shows a negative balance. Since carbon is the dominant element compared to all other elements, the loss of overall mass is reflected in the carbon balance as well. The hydrogen balance also shows a negative balance during the process. This is unexpected due to the fact that a hydrogen uptake is observed during the reaction. The two major reasons for mass loss of hydrogen were neglecting the product gas formed during the reaction and the mass lost during THF rotovaporization and vacuum distillation. This mass primarily contained lighter species and hence is richer in hydrogen

Table 4.7 Elemental composition of the hydrogenation reaction species for all the three solvents.

Solvent	Element	Fresh Solvent (%)	Product Fraction (%)			
			Pass 1 Pitch	Pass 1 THF Insolubles	Pass 1 Recovered Solvent	Pass 2 Recovered Solvent
CBB	C	91.66	92.24	78.02	91.79	90.39
	H	5.78	5.46	3.45	5.85	6.16
	N	0.00	0.56	0.86	0.00	0.00
	S	0.56	0.63	0.94	0.45	0.39
	H/C Ratio	0.75	0.71	0.53	0.77	0.82
HCO	C	92.46	92.59	77.99	93.16	93.91
	H	5.76	5.66	3.56	5.95	6.22
	N	0.76	0.85	0.99	0.81	0.74
	S	0.59	0.69	0.91	0.51	0.48
	H/C Ratio	0.75	0.73	0.55	0.77	0.80
RCO	C	91.81	92.15	76.36	89.90	89.66
	H	6.9	6.23	4.21	7.25	7.38
	N	0.58	0.52	0.98	0.72	0.61
	S	0.71	0.79	0.93	0.55	0.51
	H/C Ratio	0.9	0.81	0.66	0.96	0.99

Table 4.8 Carbon balance of the select hydrogenation runs for all the three solvents.

Run	Coal C (g)	Solvent C (g)	Total C Input (g)	Pitch C (g)	THF Ins. C (g)	Rec. Solv. C (g)	Total C Output (g)	Input - Output (g)	Loss (%)
1B	3.32	18.42	21.74	2.77	1.80	16.2	20.77	0.97	4.5
2C	3.31	18.42	21.73	3.52	1.84	15.09	20.45	1.28	5.9
3A	3.31	18.64	21.95	3.63	2.17	14.27	20.07	1.88	8.6
4B	3.31	18.72	22.03	2.87	1.85	14.08	18.8	3.23	17.2
5C	3.31	18.82	22.13	2.58	1.81	15.2	19.59	2.54	11.5
6A	3.32	18.34	21.66	2.47	2.06	14.33	18.86	2.8	12.9

Table 4.9 Hydrogen balance of the select hydrogenation runs for all the three solvents.

Run	Coal H (g)	Solvent H (g)	Total H Input (g)	Pitch H (g)	THF Ins. H (g)	Rec. Solv. H (g)	Total H Output (g)	Input - Output (g)	Loss (%)
1B	0.20	1.16	1.36	0.16	0.08	0.99	1.23	0.13	9.6
2C	0.20	1.14	1.34	0.21	0.08	0.96	1.25	0.09	6.7
3A	0.20	1.4	1.60	0.24	0.12	1.15	1.51	0.09	5.6
4B	0.20	1.19	1.39	0.17	0.08	0.96	1.21	0.18	12.9
5C	0.20	1.20	1.40	0.16	0.08	1.01	1.25	0.15	10.7
6A	0.20	1.48	1.68	0.17	0.11	1.18	1.46	0.22	13.1

compared to the other elements. As these species are not accounted for in the mass or the elemental balances, a negative hydrogen balance seems reasonable. The last three rows of both Tables 4.8 and 4.9 (i.e. runs 4B, 5C and 6A) show the carbon and hydrogen balance for the recovered solvents for the same runs as with fresh solvents. It is observed that for the same runs of fresh and recovered solvents, the recovered solvents show a higher carbon and hydrogen loss. This is consistent with the mass balances which showed higher losses for the recovered solvents.

4.7.5 Optical Texture

Optical texture was determined for both the raw pitch and the corresponding cokes obtained from the pitch in the coke yield test. The pitch samples saw a high temperature during the vacuum distillation and hence it was speculated that there might be mesophase formation during this process of heat treatment. This was the reason to study the optical texture of the raw pitches. Samples were prepared by embedding them into epoxy and then polishing them for observation under the polarized-light microscope. The optical texture was determined according to the procedure described in Section 3.3.3. This technique is very important for the coke samples as the end use of the material is determined based on the structure of the material.

The optical micrographs of the raw pitches are shown in Appendix 2. As can be seen, the majority of the pitches do, in fact, show the onset of some mesophase development. This is a consequence of the high temperature they were exposed to during the vacuum distillation. As mentioned in Section 4.7.3 above, the presence of mesophase

dispersed in the isotropic pitch matrix explains the high coke yield and moderate softening found for these pitches.

Figure 4.8 shows the optical micrographs of the cokes samples obtained from the pitches produced using fresh and recovered solvents in the hydrotreatment step. Figures 4.8 A,C, and E show the cokes obtained for pass 1 runs with fresh solvents while Figures 4.8 B,D and F show the cokes obtained for pass 2 runs for recovered solvents. All the cokes produced from the hydrogenation reactions with CBB and HCO were found to have large flow domains, which indicate an anisotropic texture. For the RCO samples, the domains appear to be smaller and more uniformly distributed suggesting a lesser degree of anisotropy as compared to the samples from CBB and HCO. It is important to note that the coke samples from pass 2 runs are very similar to the coke samples of pass 1 runs, suggesting that not much structure related differences are induced by the reaction with recovered solvents. As discussed earlier, anisotropic coke is suitable for the production of graphite electrodes or anodes while isotropic coke is more suitable for the production of nuclear graphite.

4.8 Variation of Hydrogenation Parameters

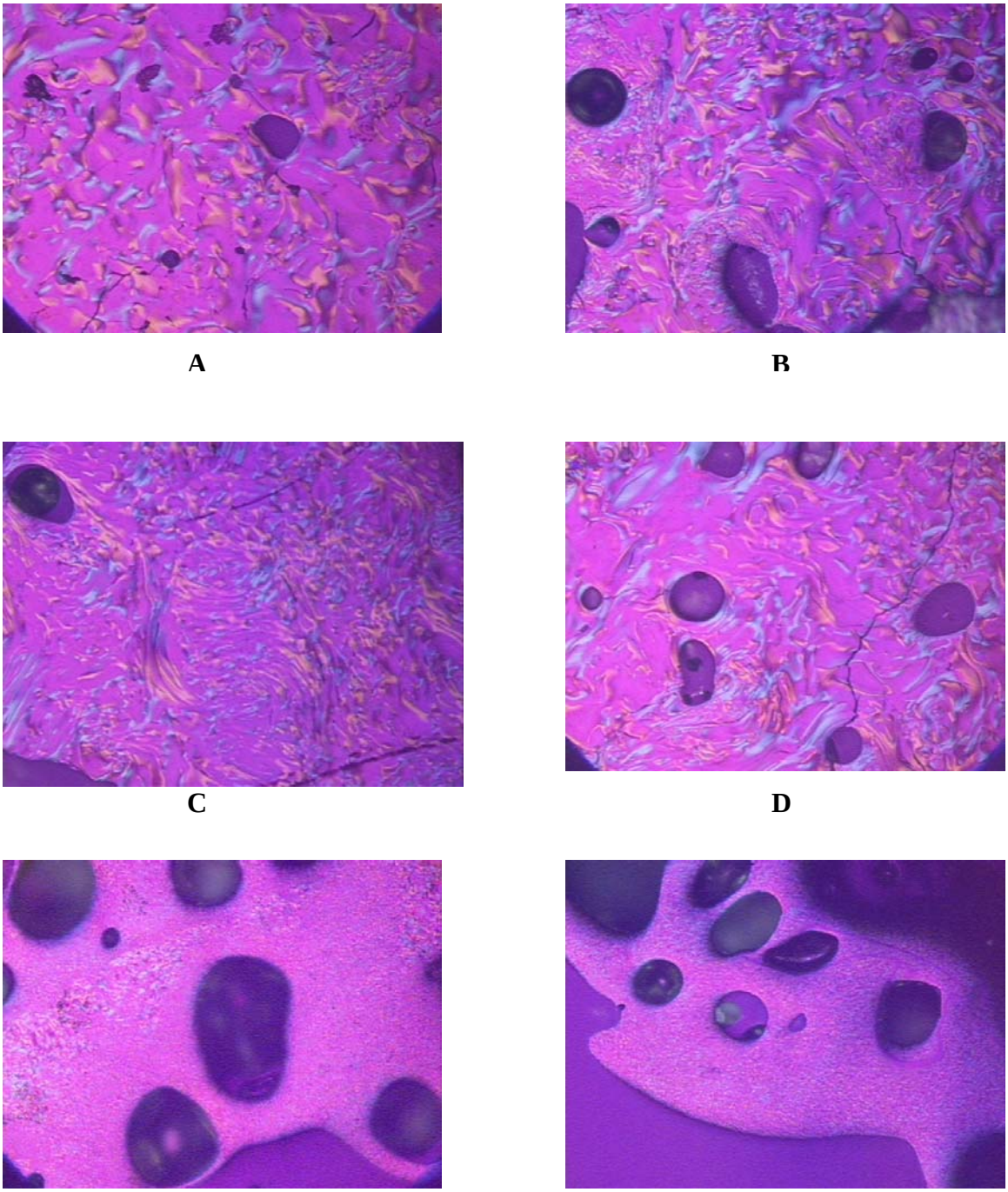
To understand the influence of the reaction parameters on hydrogenation, two important parameters were varied. These were temperature and reaction atmosphere. The other parameters such as the reaction pressure and the solvent-to-coal ratio were not studied here as they have been previously looked at in a similar work [35]. Here hydrotreatment was performed at three different temperatures, viz. 350 ^{o}C, 400 ^{o}C and 450 ^{o}C. The reaction atmosphere was changed to nitrogen instead of hydrogen at the

same standard pressure of 500 psig cold. Table 3.3 gives the details of the runs involving different hydrogenation conditions.

4.8.1 Effect of Temperature

Temperature is an important parameter in hydrogenation as it determines the severity of the hydrotreatment reaction. All the runs in which temperature was varied included CBB as the solvent along with an initial cold hydrogen pressure of 500 psig and reaction time of one hour. CBB was chosen as the solvent to study the effect of temperature as it is commercially available and gave the highest conversion among the three solvents. As mentioned earlier, conversion results were studied at three different temperatures for both fresh and recovered solvents. Temperatures above 450 ^{o}C were avoided since higher temperature would give low liquid yield due to excessive gas make by cracking.

Figure 4.9 shows the coal-alone conversion for different temperatures for the fresh and recovered CBB in the hydrogen atmosphere. As expected the conversion goes up with temperature. For the fresh CBB solvent, the lowest conversion is observed at 350 ^{o}C which is 32.1 ± 0.8 %, while the coal-alone conversion increases at higher temperatures as seen from Figure 4.9, giving 43.4 ± 0.9 % and 47.8 ± 1.2 % for 400 ^{o}C and 450 ^{o}C respectively. Figure 4.9 also shows the conversion results at the same temperatures but for the recovered solvents. Here the same trend is followed with conversion results of 32.8 ± 2 %, 44.2 ± 0.8 %, 49.4 ± 0.9 % with corresponding increasing temperatures. It should be noted that the recovered solvents show slightly higher conversion results for each corresponding temperature than the fresh solvents.



A **B**

C **D**

E **F**

Figure 4.8 Optical Micrographs of coke samples: (A) Pass 1 coke with CBB. (B) Pass 2 coke with CBB. (C) Pass 1 coke with HCO. (D) Pass 2 coke with HCO. (E) Pass 1 coke with RCO. (F) Pass 2 coke with RCO.

Also it can be noticed that the difference between the conversion at the same temperature for fresh and recovered solvent increases with temperature. In processes like EDS (discussed earlier) it has been observed that if the severity of the solvent rehydrogenation step is increased, the solvent is able to incorporate more hydrogen due to enhanced reactivity at higher temperatures. These rehydrogenated solvents are then able to perform better when reacted with coal. This trend is noted in the runs here using the recovered solvents. However, there is a trade-off. While high temperature will give high conversion, too high a temperature will cause cracking and hydrogen rich species might be lost to the vapor phase. This phenomenon may be bad as the products would be less rich in hydrogen and the conversion would also suffer. No attempt was made here to assess the effect of temperature on the gas-phase yield or composition.

Table 4.10 shows the elemental analysis of the products obtained with CBB at the three different temperatures. The hydrogen-to-carbon ratio increases in the order fresh to pass 1 recovered to pass 2 recovered solvent. The interesting point to note here is the difference in the hydrogen-to-carbon ratio between the fresh and successively hydrogenated solvents is less at low temperature than at higher temperatures. The pitch properties do not change much with temperature and exhibit similar hydrogen-to-carbon ratio. Also the THF insolubles have similar properties for different temperatures.

Figure 4.10 shows the pressure profiles for fresh and recovered solvent in a hydrogen atmosphere at 350 ^{o}C and 450 ^{o}C. The higher temperature, 450 ^{o}C, gives the maximum difference between the final and initial cold pressures whereas 350 ^{o}C gives a smaller difference. This suggests that the conversion should increase with increasing

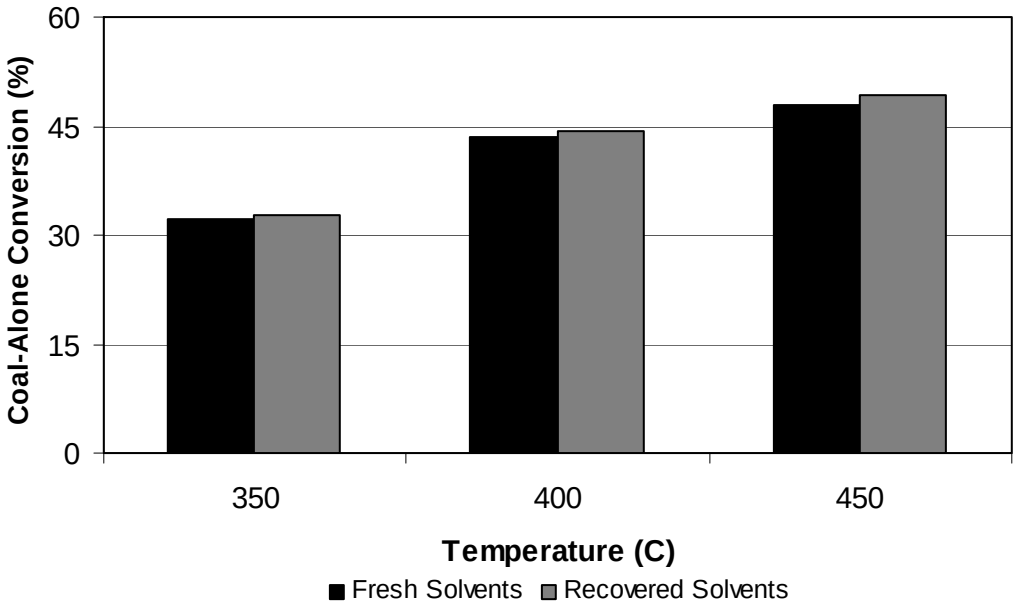


Figure 4.9 Coal-alone conversion at different temperature for fresh and recovered CBB at 500 psig cold hydrogen and one hour reaction time

temperature, due to higher hydrogen uptake by the reactants and indeed this was found to be the case.

Samples of the corresponding cokes were tested for optical texture under polarized light microscope and are shown in Figure 4.11. The results show similar texture for both 350 ^{o}C and 450 ^{o}C, that of large domains governing anisotropy with slightly smaller domains for the 350 ^{o}C samples as compared to the 450 ^{o}C samples. This suggests that lower temperature might impart less anisotropy. Overall these structures exhibit similarity to the samples at 400 ^{o}C of CBB. It must therefore follow that reaction temperature does not play a major role in modifying the structure of the cokes. Here again the samples from pass 1 and 2 do not show any difference in the coke structure.

4.8.2 Effect of Reaction Atmosphere

To study the effect of reaction atmosphere on the conversion and the nature of the products, nitrogen was used instead of the standard hydrogen atmosphere. The initial cold pressure of 500 psig was maintained for all the reactions and was not varied. The aim here was to study the effect of the gas phase on the reaction and not the pressure.

Figure 4.12 shows the coal-alone conversion for the two different atmospheres for both fresh and recovered CBB solvent at 400 ^{o}C, 500 psig cold pressure and a reaction time of one hour. It can be seen that the nitrogen atmosphere gave conversion results of 33.8 ± 0.4 % and 34.1 ± 0.7 % for fresh and recovered solvent with the corresponding conversion of 43.4 ± 0.9 % and 44.2 ± 0.8 % for the hydrogen atmosphere. The conversion decreases by around 10 % when the atmosphere is changed to nitrogen.

Table 4.10 Elemental composition of the hydrogenation reaction species for CBB at all the three temperatures.

Temperature (^{o}C)	Element	Fresh Solvent (%)	Product Fraction (%)			
			Pass 1 Pitch	Pass 1 THF Insolubles	Pass 1 Recovered Solvent	Pass 2 Recovered Solvent
350	C	91.66	92.12	78.71	92.12	92.88
	H	5.78	5.56	3.51	5.91	6.09
	N	0.71	0.88	0.92	0.77	0.75
	S	0.56	0.71	0.93	0.5	0.47
	H/C Ratio	0.75	0.72	0.53	0.77	0.78
400	C	91.66	92.24	78.02	91.79	90.39
	H	5.78	5.46	3.45	5.85	6.16
	N	0.71	0.56	0.86	0.00	0.00
	S	0.56	0.63	0.94	0.45	0.39
	H/C Ratio	0.75	0.71	0.53	0.77	0.82
450	C	91.66	92.15	75.22	90.90	90.56
	H	5.78	5.49	3.49	6.21	6.48
	N	0.71	0.51	0.97	0.73	0.68
	S	0.56	0.74	0.89	0.45	0.36
	H/C Ratio	0.75	0.72	0.56	0.82	0.86

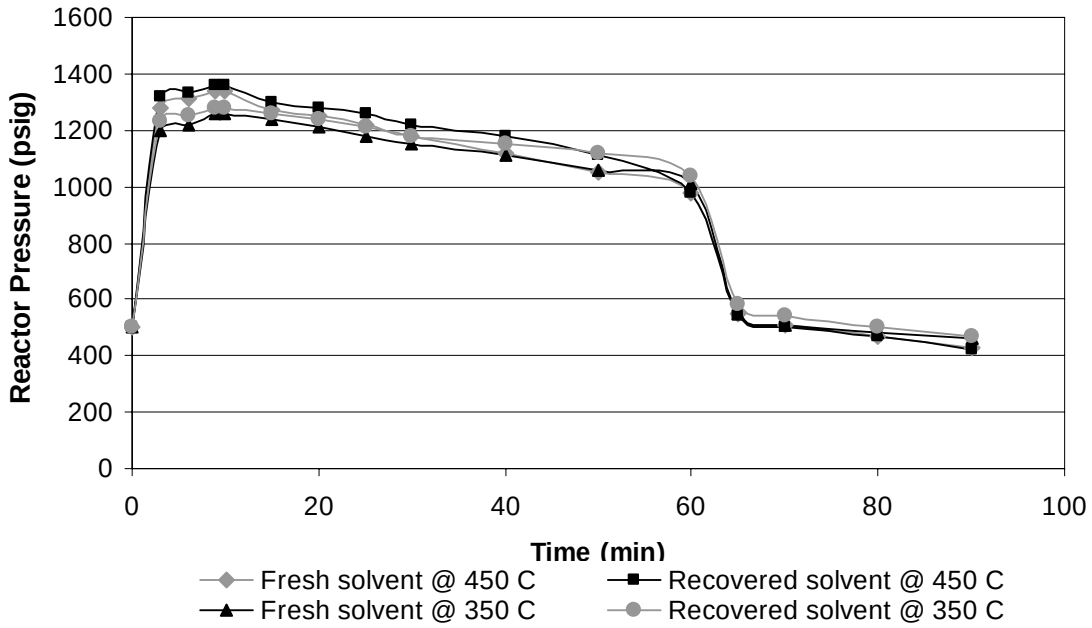
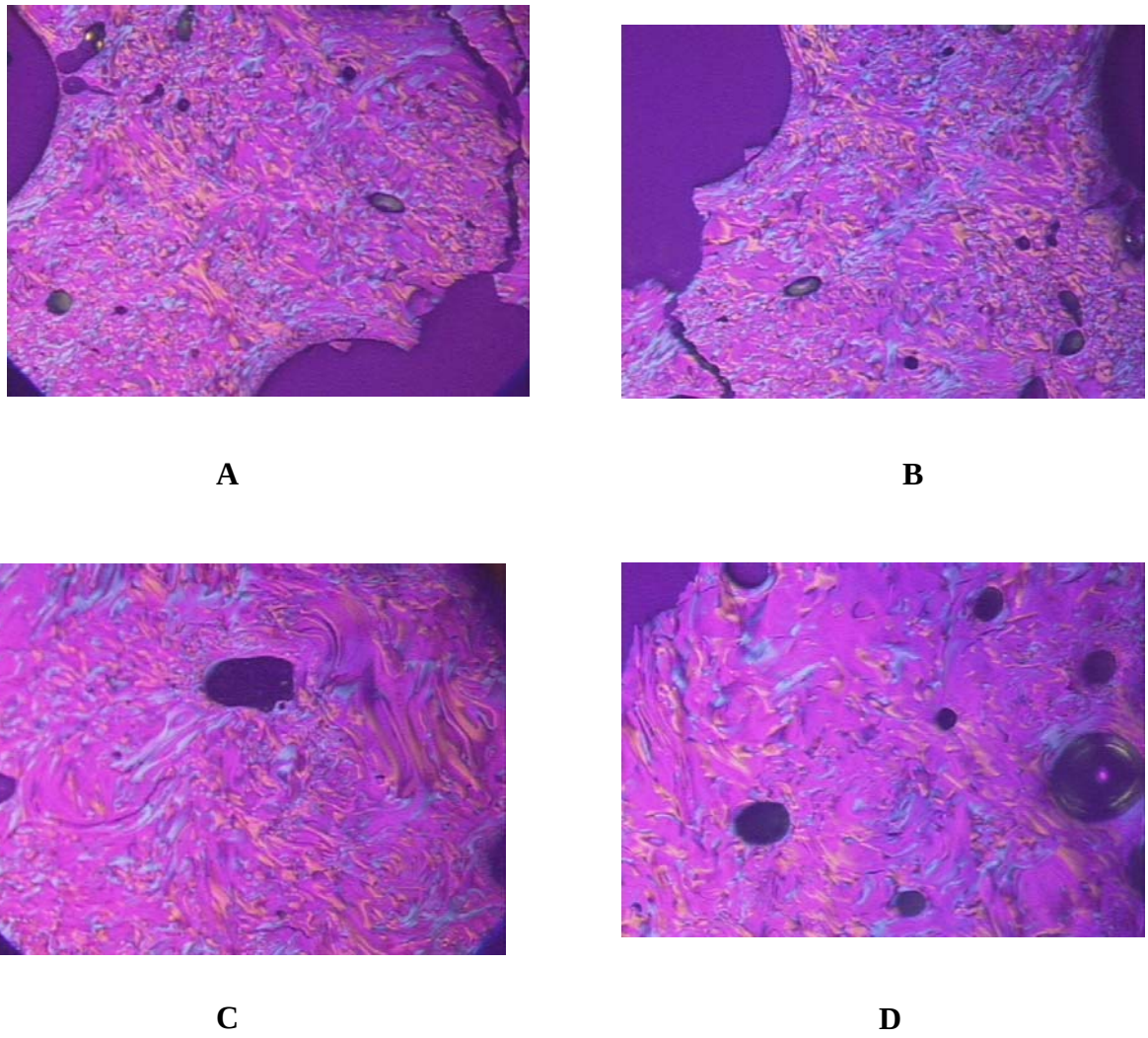


Figure 4.10 Pressure profiles at 450 ^{o}C and 350 ^{o}C for fresh and recovered CBB at 500 psig cold hydrogen and reaction time of one hour.



A **B**

C **D**

Figure 4.11 Optical micrographs of coke samples: (A) Pass 1 coke at 350 ^{o}C. (B) Pass 2 coke at 350 ^{o}C. (C) Pass 1 coke at 450 ^{o}C. (D) Pass 2 coke at 450 ^{o}C.

This suggests that hydrogen is critical during these hydrogenation runs. There is also one more important thing to notice here. The conversion with nitrogen at 400 ^{o}C is higher than at 350 ^{o}C with hydrogen. Which means that though the hydrogen atmosphere is crucial, it is the temperature which plays a major role in these types of reactions. Also here the difference in conversion for fresh and recovered solvent is very small. It is unexpected to see that the conversion is almost the same between fresh and recovered solvents even in the absence of gaseous hydrogen. In reactions such as these, where there is deficiency of hydrogen either by absence of gas phase hydrogen or by absence of hydroaromatic structures in the solvent, the shuttling effect becomes the main mechanism for hydrogen transfer. This effect is described in detail in Section 2.5.4.

Though the shuttling effect may be occurring in reactions involving a hydrogen atmosphere, it is not dominant. However, it should become dominant during reaction in the absence of hydrogen. Primarily two or three ring aromatics species like naphthalene, anthracene and phenanthrene have been found to be responsible for shuttling. These species were found to increase from fresh solvent to recovered solvents under either hydrogen or nitrogen, and even at higher temperatures. These data are shown in Table 4.11 for fresh and recovered CBB samples under different conditions. The data were obtained from Koppers Industries laboratories and were performed by GC for the polyaromatic hydrocarbons (PAH) content. These data give the content of two, three and higher ring aromatic species in the solvents. Based on the data it can be said that the comparable conversion (between fresh and recovered solvents) during reactions with a nitrogen atmosphere is primarily due to the shuttling effect by these aromatic species.

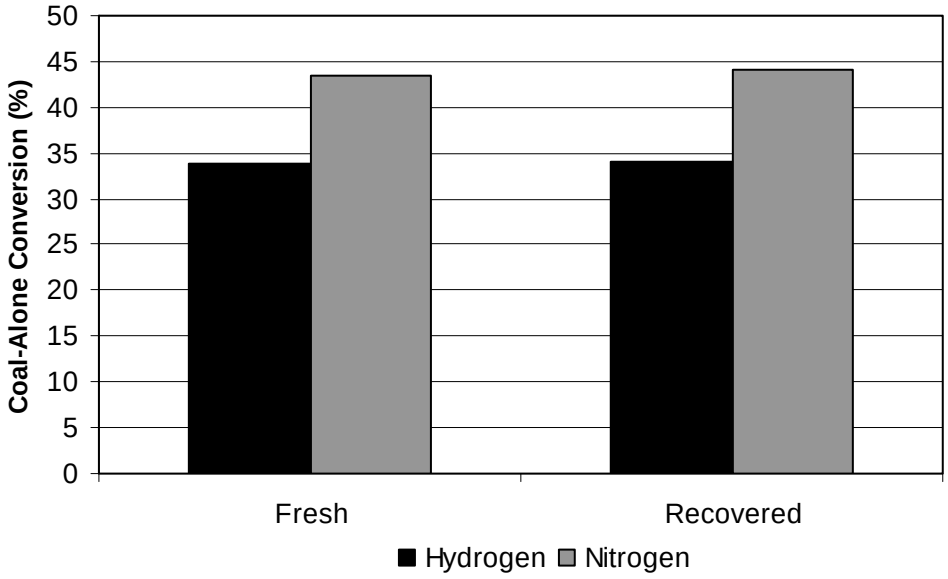


Figure 4.12 Coal-alone conversion for fresh and recovered CBB under different reaction atmospheres and 400 ^{o}C, 500 psig cold pressure and a reaction time of one hour.

Figure 4.13 shows the pressure profiles for reaction of coal with fresh and recovered CBB solvent under a nitrogen atmosphere. As discussed earlier it shows a rate of rise at the reaction temperature unlike that seen for the hydrogen atmosphere. Here the final pressure is slightly higher than the initial cold pressure as there is no consumption of inert nitrogen. In fact the final and the initial pressures are nearly identical indicating little generation of gas-phase organics.

Table 4.12 shows elemental analysis of the hydrogenation products from reactions involving the nitrogen atmosphere. The recovered solvent here also shows an increase in hydrogen content compared to fresh solvent, which indeed proves that some light organic species must be produced during such reactions even if a reactive atmosphere is not employed. The interesting point to observe is that the difference between the hydrogen content of the recovered and fresh solvent, is far less compared to those involving the reactive hydrogen atmosphere. The pitch and the THF insolubles properties do not change appreciably.

Coke samples from the pitches produced in the nitrogen atmosphere were studied for optical texture. In Figure 4.14, these results are compared with the analogous samples obtained from the hydrogen atmosphere. The domains for the cokes from the nitrogen atmosphere appear smaller than those in the samples reacted under hydrogen. It can be inferred that the domain growth under nitrogen has occurred but to a much lesser extent than that observed for hydrogen. Hence the cokes from the nitrogen atmosphere appear to be more isotropic in nature. This may be important as it allows further control over the structure of the resultant cokes. The pitch samples shown in Appendix 2 do not show any appreciable growth of mesophase as observed for the other samples.

Table 4.11 PAH species in fresh and recovered CBB at various conditions of temperature and reaction atmosphere.

Sample	Fresh (%)	Recovered at 350 ^{o}C (%)	Recovered at 400 ^{o}C (%)	Recovered at 450 ^{o}C (%)	Recovered at 400 ^{o}C & N_2 (%)
Naphthalene	2.53	3.79	5.75	7.07	5.47
Acenaphthylene	0.04	0.17	0.37	0.5	0.31
Acenaphthene	4.57	4.22	4.61	4.89	4.32
Phenanthrene	14.63	15.45	15.82	16.05	15.56
Anthracene	1.07	1.09	1.45	1.49	1.15

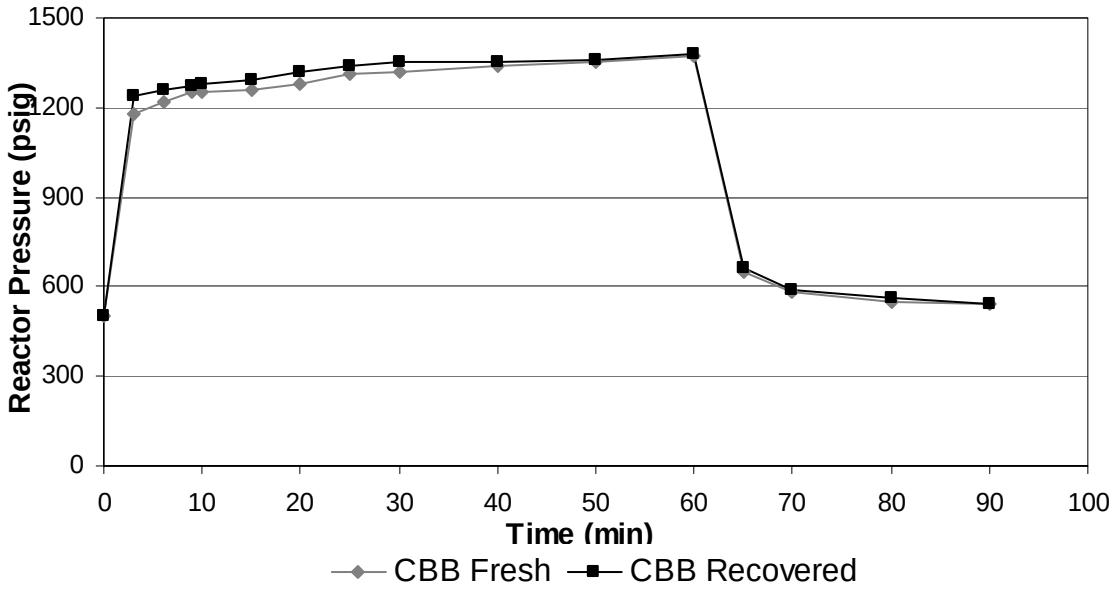


Figure 4.13 Pressure profiles for fresh and recovered CBB under 500 psig cold nitrogen at 400 ^{o}C for one hour.

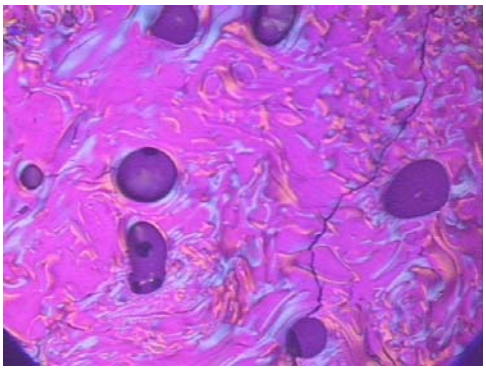
4.9 Successive Hydrogenation Runs

Two different types of successive hydrogenation runs were performed to investigate the effect of successive recycle of the recovered solvent on the process conversion. This can be important industrially where consecutive batches of hydrogenation reactions would be performed in which part of the solvent is recycled. In the first method, conversion with only recycled solvents was studied. Since there was a mass loss everytime the run was performed, the amount of coal had to be decreased for each subsequent run to maintain the same solvent-to-coal ratio. For this purpose the vacuum distillation was carried out at higher temperatures around 300 ^{o}C so as to maximize the amount of solvent recovered as a distillate product.

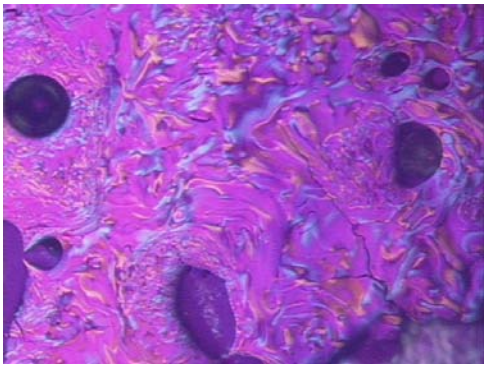
In the second method, a predetermined fixed quantity of fresh solvent was added to the recycled solvent to maintain both the solvent-to-coal ratio and the mass of solvent for each run. The added quantity of fresh solvent was increased in a predetermined manner with each subsequent run. Here the mass of coal was held constant and did not have to be decreased. These reactions were run at 400 ^{o}C and 500 psig cold hydrogen. The rationale for doing these latter experiments was to assess the effect of increasing PAH's (with increasing amount of fresh solvent) on the coal-alone conversion when the original PAH content would decrease with successive recycling in the recovered solvents. The effect of PAH's and hydroaromatics on conversion is explained in more detail in the following section. The quantities of coal and the recovered solvent are shown in Table A.10 for method one while the quantities of fresh and recovered solvents are shown in Table A.11.

Table 4.12 Elemental composition of the hydrogenation reaction species for CBB under hydrogen and nitrogen.

Atmosphere	Element	Fresh Solvent (%)	Product Fraction (%)			
			Pass 1 Pitch	Pass 1 THF Insolubles	Pass 1 Recovered Solvent	Pass 2 Recovered Solvent
Hydrogen	C	91.66	92.24	78.02	91.79	90.39
	H	5.78	5.46	3.45	5.85	6.16
	N	0.71	0.56	0.86	0.56	0.44
	S	0.56	0.63	0.94	0.45	0.39
	H/C Ratio	0.75	0.71	0.53	0.77	0.82
Nitrogen	C	91.66	92.56	78.12	92.16	92.91
	H	5.78	5.42	3.56	5.82	5.98
	N	0.71	0.85	0.99	0.64	0.59
	S	0.56	0.74	0.94	0.49	0.47
	H/C Ratio	0.75	0.70	0.55	0.76	0.77



A



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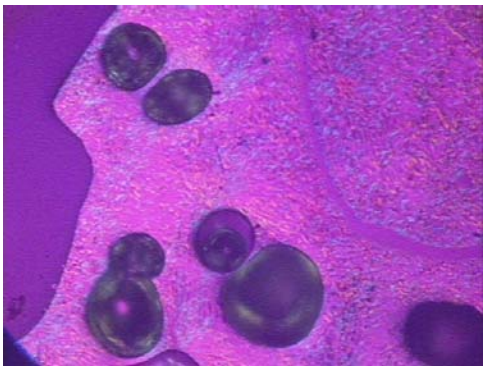

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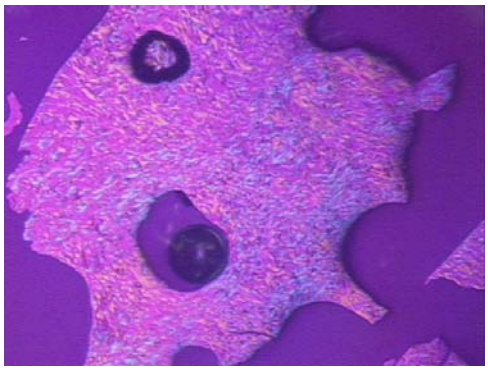

D

Figure 4.14 Optical Micrographs of coke samples: (A) Pass 1 coke under H_2. (B) Pass 2 coke under H_2. (C) Pass 1 coke under N_2. (D) Pass 2 coke under N_2.

Figure 4.15 shows the conversion results for method one for each subsequent pass from pass 1 (fresh solvent) to pass 5 (recycled through four successive hydrogenation runs). No make-up solvent was added in these runs. The reactions were stopped at pass 5 as with more passes the amount of coal and solvent decreases to a point where accurate conversion results are difficult to achieve. The conversion attains a maximum and then starts to decrease after the third pass. The difference between the last pass (pass 5) and that with the fresh solvent (pass 1) is not great and it is expected that the conversion would continue to drop with more subsequent passes. This can be explained based on the following hypothesis as suggested by A. Awadalla et al. [36]. Initially fresh coal-derived solvent contains mostly polyaromatic hydrocarbons (PAH) with some hydroaromatics and alicyclics. It is known that hydroaromatics are good hydrogen donors whereas PAH's are good shuttlers. The initial content of PAH's in such typical coal-derived solvents exceeds that of the content of hydroaromatics. This is the primary reason why these coal derived solvents are poor hydrogen donors and give low conversion compared to standard H-donor solvents like tetralin. During the process of hydrogenation some of the heavy PAH's are converted to corresponding hydroaromatics. Upon repetitive or severe hydrogenation, these hydroaromatics would inturn be converted to alicyclics, which do not serve any purpose with respect to the hydrogenation reactions. So, during the third pass when the conversion peaks, the concentration of hydroaromatics must be maximum after which they start to convert into alicyclics and hence the conversion drops. Thus it is speculated that with further hydrogenations after the fifth pass, the conversion might drop beyond that of the starting fresh solvent, because most of the PAH's and hydroaromatics

would have converted to alicyclics. This hypothesis could be confirmed by GC analysis on the successively recovered solvents but it was beyond the scope of the present work.

Figure 4.16 follows the conversion with hydrogen content of the recovered solvent for successive hydrogenations. Here the same maximum in conversion is observed. This shows that when the solvent is going through the conversions of PAH's into hydroaromatics and hydroaromatics to alicyclics, the hydrogen content of the recovered solvents goes up. However the increased hydrogen content does not guarantee an increase of conversion with subsequent hydrogenation runs since now the hydrogen is bound up in the relatively unreactive alicyclics. The curve also shows a decreasing trend for the final runs, indicating that the conversion may equalize or even drop below the initial conversion at some point of time upon continued solvent recycle.

In the second method, blends of fresh and successively recovered solvents were used to determine the conversion yields for CBB solvent at 400 ^{o}C and 500 psig cold hydrogen pressure. Figure 4.17 shows the conversion yield when the successively recovered solvent was blended with fresh make-up solvent to keep the absolute mass of solvent constant in each run. This blend was then incorporated in subsequent hydrogenation runs. The recovered solvent in each subsequent run is obtained from the preceding hydrogenation run and is not a once through recovered solvent. Since each subsequent run had recovered solvent in the blend, the mass losses were observed to first increase and eventually stabilize with increasing amounts of fresh make-up. However the make-up was increased in a predetermined manner from 20 to 80 % to observe if some appreciable conversion changes would occur.

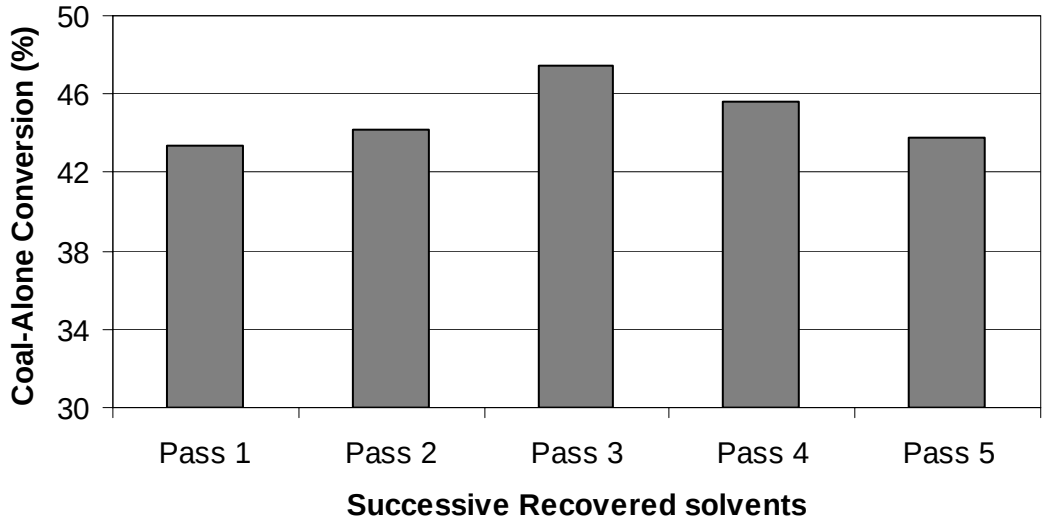

Figure 4.15 Successive recovered solvent conversion at 400 ^{o}C, 500 psig cold hydrogen and one hour reaction time and no make-up solvent added.

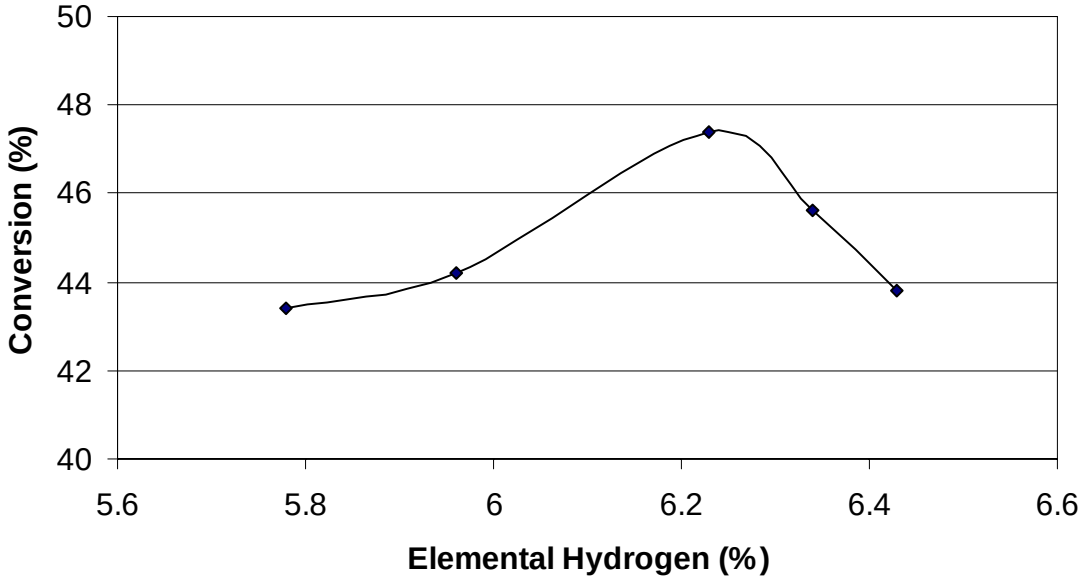

Figure 4.16 Variation of successive recovered conversion with elemental hydrogen content of the recovered solvent.

Figure 4.17 shows that the conversion goes through a maximum before starting to decrease as increasing amounts of fresh make-up solvent are added in subsequent runs. Here the conversion in the later runs is not dropping like that in the first method but is flattening out and achieving a steady value. Unlike the results of method one, the introduction of fresh solvent with the recovered solvent is maintaining the concentration of species like PAH's and hydroaromatics roughly constant in the blend giving more conversion at each pass. Also, since the concentration of these important species continues to increase with the introduction of more and more fresh solvent, the conversion does not show a decreasing trend but stabilizes to a value close to that found when 100 % fresh solvent is employed. There is one important thing to observe from Figure 4.17 where the curve shows a rise in conversion in the 0-20 % make-up range. In an actual continuous process, a make-up of fresh solvent between 0 to 20 % might be reasonably expected. After the initial variations in the conversion, the amount of fresh solvent make-up in the process will eventually stabilize. If the process is such that the losses are around 20 %, a high coal-alone conversion can be expected. This increased incremental conversion could have a major impact on the economics of such a process.

Figure 4.18 shows the conversion profile with the hydrogen content of the blends. It can be seen that the conversion profile follows the same trend as before with increasing hydrogen content. The same argument as for method one applies here too, that increasing hydrogen uptake by the blends does not necessarily imply an increase in conversion.

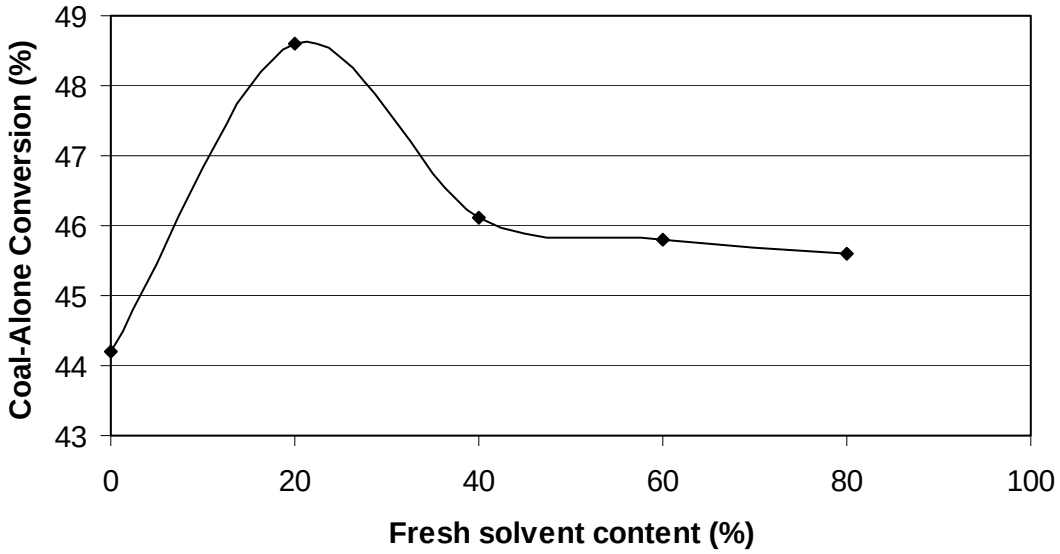

Figure 4.17 Coal-alone conversion results for fresh and successively recovered solvents blends at 400 ^{o}C, 500 psig cold hydrogen and one hour reaction time.

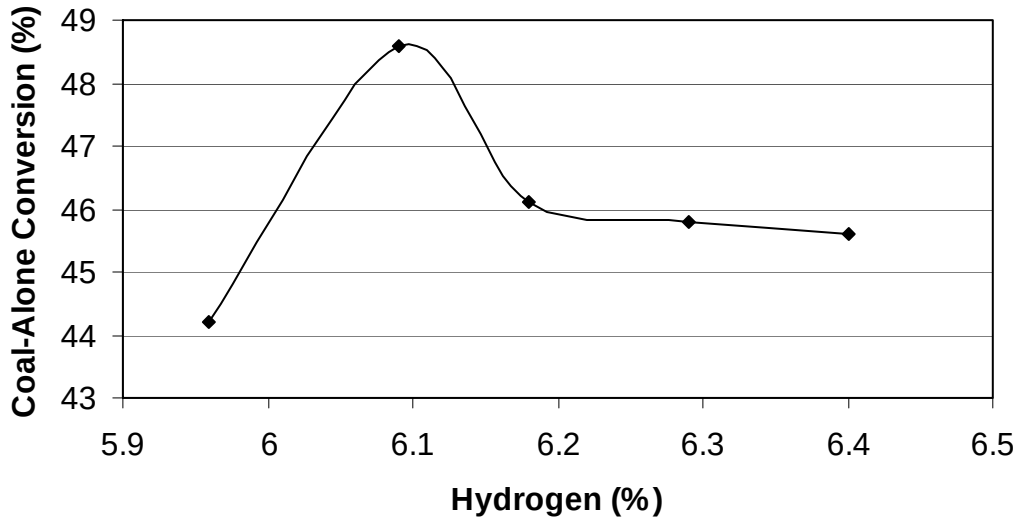

Figure 4.18 Variation of coal-alone conversion for fresh and successively recovered solvents blends with elemental hydrogen content of the blends.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Based on the results of the hydrotreatment runs performed on coal in the presence of three different coal-derived solvents and the properties of the pitches obtained from these runs, several conclusions could be drawn which are summerized as follows:

1. The overall conversion does not give a true comparison between the different solvents due to the large solvent-to-coal ratio employed in these experiments. The coal-alone conversion allows a better means of differentiating the efficacy of each solvent.
2. Based upon the coal-alone conversion, the coal-derived solvent CBB gives the highest conversion followed by HCO and RCO at 400 ^{o}C, 500 psig cold hydrogen and one hour reaction time.
3. The recovered solvents from the process give comparable coal-alone conversions as compared to their respective fresh solvents in producing THF solubles for the same reaction conditions.
4. The coal-alone conversion is highly dependent on the reaction temperature and the composition of the gaseous atmosphere. Higher temperature and a hydrogen atmosphere give the best conversion.
5. The pitch product showed a higher hydrogen-to-carbon ratio than the starting coal, suggesting an addition of hydrogen to the coal matrix. The hydrogen-to-

carbon ratios for pitches produced with different solvents were found to be similar. The ash content for all the pitches was on the order of 0.2 %.

6. The yield of pitch from the process was found to vary between 14.6 to 64.6 % based on the amount of solvent recovered in the vacuum distillation.
7. The recovered solvents showed higher hydrogen-to-carbon ratio than the starting fresh solvents which could be the primary reason for their comparable performance to the fresh solvents.
8. The quantity of solvent distilled from the product mixture had a dramatic effect on the softening point and coke yield of the resultant pitch. The softening point and the coke yield demonstrate a linear relationship with each other. This is important for the manufacture of tailor-made pitches with desired properties.
9. The optical texture of the cokes from the pitches was found to be anisotropic. The cokes from the pitches for reactions with fresh and recovered solvents were found to exhibit similar optical properties.
10. Successively recovered solvents, when used alone in the hydrotreatment runs, showed that the coal-alone conversion passes through a maximum and then decreases slightly. It is speculated that, with continued solvent recycle, the decreasing trend in conversion might fall below that observed for the starting fresh solvent.
11. Blends of successively recovered and fresh solvents also showed the coal-alone conversion passing through a maximum. The conversion drops in the final stages but eventually attains a steady value as more fresh solvent was added to the blend. This can be important industrially in a continuous hydrotreatment plant where

recovered solvents are recycled to the process and blended with some fixed amount of fresh make-up solvent. Once a set process is determined for its solvent losses, the conversion can be found from data like those presented in Figure 4.17.

5.2 Recommendations for Future work

Based on the outcomes of this work, a few recommendations for future work are listed here:

1. The experiments done in this work are bench scale, wherein it is difficult to get enough pitch to perform extensive characterization. Analytical techniques such as viscocity measurements, NMR, FTIR and GC could be helpful in more fully understanding the chemistry of the products. Thus the hydrotreatment process should be done on a larger scale so that the necessary quantities of pitch and recovered solvents are available for testing. In addition a lower and more realistic solvent-to-coal ratio could then be tested.
2. The work done here did not involve external catalysts during the hydrotretament reaction. Such catalysts like Nikel-Molybedenum, iron etc. have been shown to enhance the performance of the coal-derived solvents. Hence usage of external catalysts could be envisaged for these type of reactions. Two different approaches could be utilized. First catalysts can be added to the coal-solvent mixture itself and the reaction can be run. A second approach would be utilize a separate catalytic hydrogenation step for the solvent and then use these rehydrogenated solvents on the coal, much like the EDS process.

3. The method two experiment involving increasing amounts of fresh make-up solvent can be varied slightly. Instead of using increasing predetermined amounts of fresh make-up, only the amount needed to compensate for the solvent losses could be made-up with fresh solvent. After the process stabilizes a fixed value of losses should be approached. Then from data like those in Figure 4.17, the steady-state conversion can be determined. This would be helpful for a continuous hydrotreatment process incorporating recycle solvents.

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APPENDIX 1

EXPERIMENTAL RAW DATA

Table A.1 Overall conversion of all three fresh and recovered solvents at 400 ^{o}C, 500 psig cold hydrogen pressure and one hour reaction time.

Solvent	Overall Conversion (%)
Fresh CBB	90.2
Fresh HCO	90.1
Fresh RCO	88.2
Recovered CBB	90.4
Recovered HCO	90.2
Recovered RCO	88.3

Table A.2 Coal-alone conversion of all three fresh and recovered solvents at 400 ^{o}C, 500 psig cold hydrogen pressure and one hour reaction time.

Solvent	Coal-Alone Conversion (%)
Fresh CBB	43.4 ± 0.9
Fresh HCO	42.6 ± 0.7
Fresh RCO	31.1 ± 0.5
Recovered CBB	44.2 ± 0.8
Recovered HCO	43.4 ± 1.1
Recovered RCO	33.2 ± 1.3

Table A.3 Pressure-Time data for all three fresh and recovered solvents at 400 ^{o}C, 500 psig cold hydrogen pressure and one hour reaction time.

Time (min)	Reactor Pressure (psig)					
	Fresh			Recovered		
	CBB	HCO	RCO	CBB	HCO	RCO
0	500	500	500	500	500	500
3	1150	1150	1200	1250	1250	1320
6	1200	1210	1250	1270	1290	1340
9	1220	1230	1280	1310	1330	1360
10	1220	1230	1280	1310	1330	1360
15	1200	1200	1240	1250	1260	1320
20	1180	1180	1200	1210	1220	1280
25	1120	1110	1180	1160	1150	1220
30	1100	1080	1150	1110	1090	1160
40	1060	1030	1090	1060	1040	1110
50	1030	990	1020	1030	1000	1040
60	980	950	990	980	960	990
65	550	550	600	550	550	610
70	520	530	560	510	510	550
80	490	490	520	480	480	510
90	440	450	470	430	440	460

Table A.4 Product distribution for all three fresh and recovered solvents at 400 ^{o}C, 500 psig cold hydrogen pressure and one hour reaction time.

Sample	Product Distribution (%)		
	Pitch	THF Insolubles	Recovered Solvent
CBB Fresh	11.5	9.8	71
HCO Fresh	13	9.9	69.9
RCO Fresh	16.8	11.7	64.1
CBB Recovered	12.7	9.7	66
HCO Recovered	12.2	9.8	66.7
RCO Recovered	12.2	11.4	63.5

Table A.5 Percent solvent distilled, coke yield and softening point data for all three fresh and recovered solvents at 400 ^{o}C, 500 psig cold hydrogen pressure and one hour reaction time.

Solvent	Percent of Solvent Distilled (%)	Coke Yield (%)	Softening Point (^{o}C)
CBB	41.26	59.4	88
	58.56	72.5	102
	80.22	81.4	129
HCO	39.31	60.1	86
	59.11	69.3	98
	80.15	79.1	122
RCO	40.96	62.2	92
	61.23	78.6	122
	80.2	84.1	158

Table A.6 Coal-alone conversion with temperature for fresh and recovered CBB at 500 psig cold hydrogen pressure and one hour reaction time.

Temperature (^oC)	Coal-Alone Conversion (%)	
	Fresh CBB	Recovered CBB
350	32.1 ± 0.8	32.8 ± 2
400	43.4 ± 0.9	44.2 ± 0.8
450	47.8 ± 1.2	49.4 ± 1.4

Table A.7 Pressure-Time data with temperature for fresh and recovered CBB at 500 psig cold hydrogen pressure and one hour reaction time.

Time (min)	Reactor Pressure (psig)			
	350 ^{o}C		450 ^{o}C	
	Fresh	Recovered	Fresh	Recovered
0	500	500	500	500
3	1200	1230	1280	1320
6	1220	1250	1310	1330
9	1260	1280	1340	1360
10	1260	1280	1340	1360
15	1240	1260	1270	1300
20	1210	1240	1250	1280
25	1180	1210	1220	1260
30	1150	1180	1180	1220
40	1110	1150	1120	1180
50	1060	1120	1050	1110
60	1010	1040	980	980
65	550	580	550	540
70	510	540	510	500
80	480	500	470	470
90	460	470	430	420

Table A.8 Coal-alone conversion under different reaction atmosphere for fresh and recovered CBB at 400 ^{o}C, 500 psig cold pressure and one hour reaction time.

Atmosphere	Coal-Alone Conversion (%)	
	Fresh CBB	Recovered CBB
Nitrogen	33.8 ± 0.4	34.1 ± 0.7
Hydrogen	43.4 ± 0.9	44.2 ± 0.8

Table A.9 Pressure-Time data under nitrogen for fresh and recovered CBB at 400 ^{o}C, 500 psig cold pressure and one hour reaction time.

Time (min)	Reactor Pressure (psig)	
	Nitrogen	
	Fresh	Recovered
0	500	500
3	1180	1240
6	1220	1260
9	1250	1270
10	1250	1280
15	1260	1290
20	1280	1320
25	1310	1340
30	1320	1350
40	1340	1350
50	1350	1360
60	1370	1380
65	650	660
70	580	590
80	550	560
90	540	540

Table A.10 Amount of Coal and solvent, H-content and Coal-alone conversion for Successively recovered CBB at 400 ^{o}C, 500 psig cold hydrogen pressure and one hour reaction time.

Pass No.	Coal Amount (gms)	Solvent Amount (gms)	H Content (%)	Coal-Alone Conversion (%)
Pass 1	4.003	20.12	5.78	43.4
Pass 2	3.616	18.08	5.96	44.2
Pass 3	3.226	16.06	6.23	47.4
Pass 4	2.791	13.86	6.34	45.6
Pass 5	2.362	11.81	6.43	43.8

Table A.11 Amount of fresh and recovered solvent, H-content and Coal-alone conversion for fresh/recovered CBB blends at 400 ^{o}C, 500 psig cold hydrogen pressure and one hour reaction time.

Fresh Make-up (%)	Fresh Solvent Amount (gms)	Recovered Solvent Amount (gms)	H Content (%)	Coal-Alone Conversion (%)
0	0	20	5.96	44.2
20	4.01	16.05	6.09	48.6
40	8.02	12.08	6.18	46.1
60	11.98	8.12	6.29	45.8
80	15.86	4.16	6.40	45.6

APPENDIX 2

OPTICAL MICROGRAPHS OF PITCHES

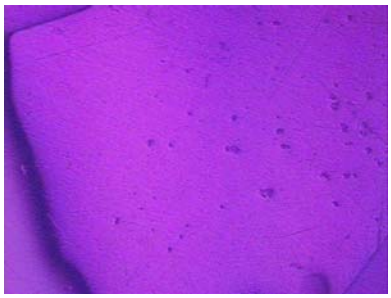

Figure A.1 Optical micrograph of pitch sample with fresh CBB at 400 ^{o}C, 500 psig cold hydrogen, 5/1 solvent-to-coal ratio and one hour reaction time.

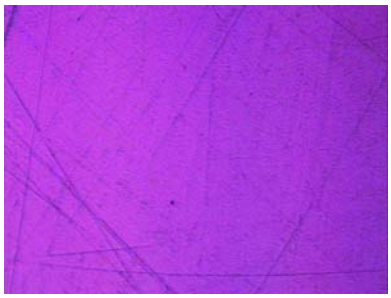

Figure A.2 Optical micrograph of pitch sample with fresh HCO at 400 ^{o}C, 500 psig cold hydrogen, 5/1 solvent-to-coal ratio and one hour reaction time.

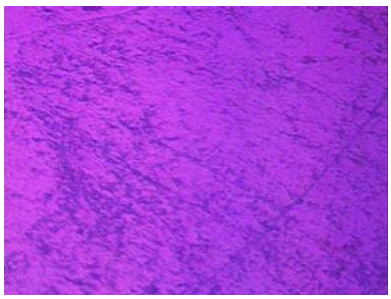

Figure A.3 Optical micrograph of pitch sample with fresh RCO at 400 ^{o}C, 500 psig cold hydrogen, 5/1 solvent-to-coal ratio and one hour reaction time.

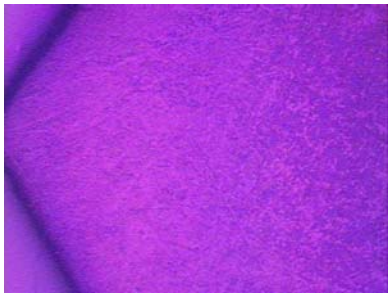

Figure A.4 Optical micrograph of pitch sample with recovered CBB at 400 ^{o}C, 500 psig cold hydrogen, 5/1 solvent-to-coal ratio and one hour reaction time.

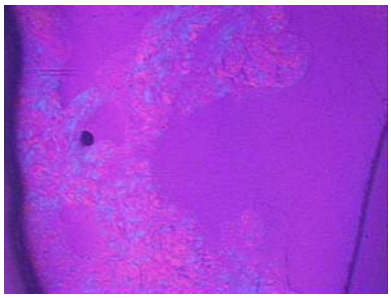

Figure A.5 Optical micrograph of pitch sample with recovered HCO at 400 ^{o}C, 500 psig cold hydrogen, 5/1 solvent-to-coal ratio and one hour reaction time.

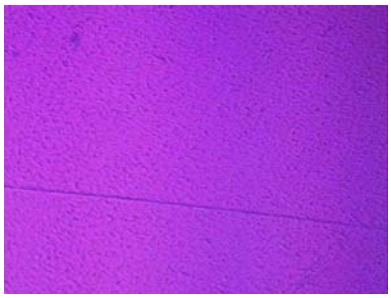

Figure A.6 Optical micrograph of pitch sample with recovered RCO at 400 ^{o}C, 500 psig cold hydrogen, 5/1 solvent-to-coal ratio and one hour reaction time.

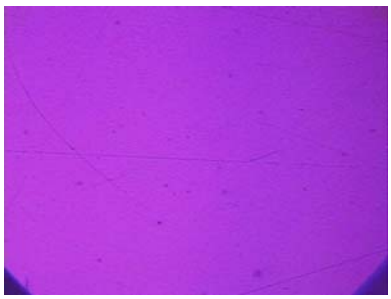

Figure A.7 Optical micrograph of pitch sample with fresh CBB at 350 ^{o}C, 500 psig cold hydrogen, 5/1 solvent-to-coal ratio and one hour reaction time.

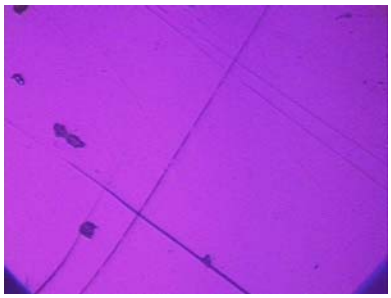

Figure A.8 Optical micrograph of pitch sample with recovered CBB at 350 ^{o}C, 500 psig cold hydrogen, 5/1 solvent-to-coal ratio and one hour reaction time.

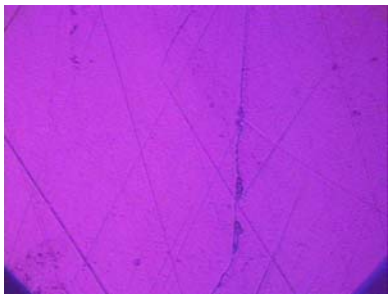

Figure A.9 Optical micrograph of pitch sample with fresh CBB at 450 ^{o}C, 500 psig cold hydrogen, 5/1 solvent-to-coal ratio and one hour reaction time.

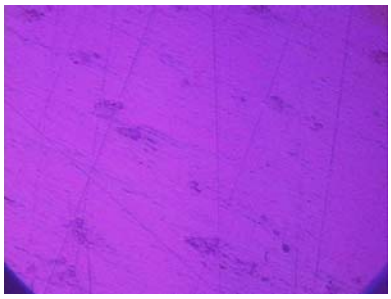

Figure A.10 Optical micrograph of pitch sample with recovered CBB at 450 ^{o}C, 500 psig cold hydrogen, 5/1 solvent-to-coal ratio and one hour reaction time.

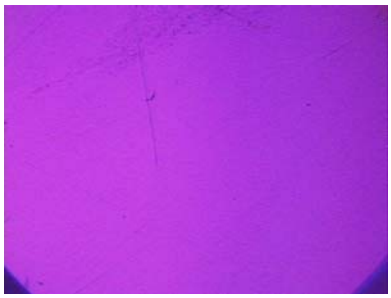

Figure A.11 Optical micrograph of pitch sample with fresh CBB at 400 ^{o}C, 500 psig cold nitrogen, 5/1 solvent-to-coal ratio and one hour reaction time.

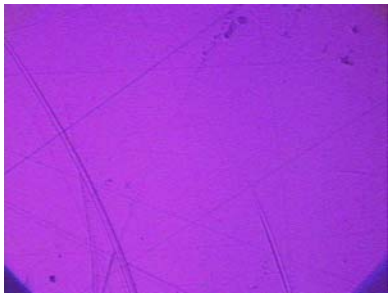

Figure A.12 Optical micrograph of pitch sample with recovered CBB at 400 ^{o}C, 500 psig cold nitrogen, 5/1 solvent-to-coal ratio and one hour reaction time.